PROCEEDINGS

from the

Green Chemistry Postgraduate Summer School online, Venice 2020

Green Sciences For Sustainable
Development Foundation

COLLECTION OF ABSTRACTS

Editors: Pietro Tundo and Aurelia Visa

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GREEN SCIENCES FOR SUSTAINABLE DEVELOPMENT FOUNDATION

100 IUPAC

Università Ca'Foscari Venezia
Dipartimento di Scienze Ambientali, Informatica e Statistica

GREEN CHEMISTRY ONLINE POSTGRADUATE SUMMER SCHOOL

6-10 July 2020
Venice, Italy

Organizers:
Pietro Tundo Chairman
Fabio Aricò
Aurelia Visa
Elena Alfine
Emilia G. Pasta

Topics:
Exploitation of renewable resources
New reaction pathways
Energy saving
Food security
Green Chemistry for cultural heritage
Climate Change mitigation

Info at **www.unive.it/ssgc**

The Editors would like to thank Elena Alfine and Emilia Pasta for their support in the creation of this book.

JULY 6-10, 2020 – ONLINE

Organized by

GREEN SCIENCES
FOR SUSTAINABLE
DEVELOPMENT
FOUNDATION

In collaboration with

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

Ca' Foscari
University
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Cultural Organization
Network "Green Chemistry Excellence
from the Baltic Sea to
the Mediterranean Sea and Beyond"

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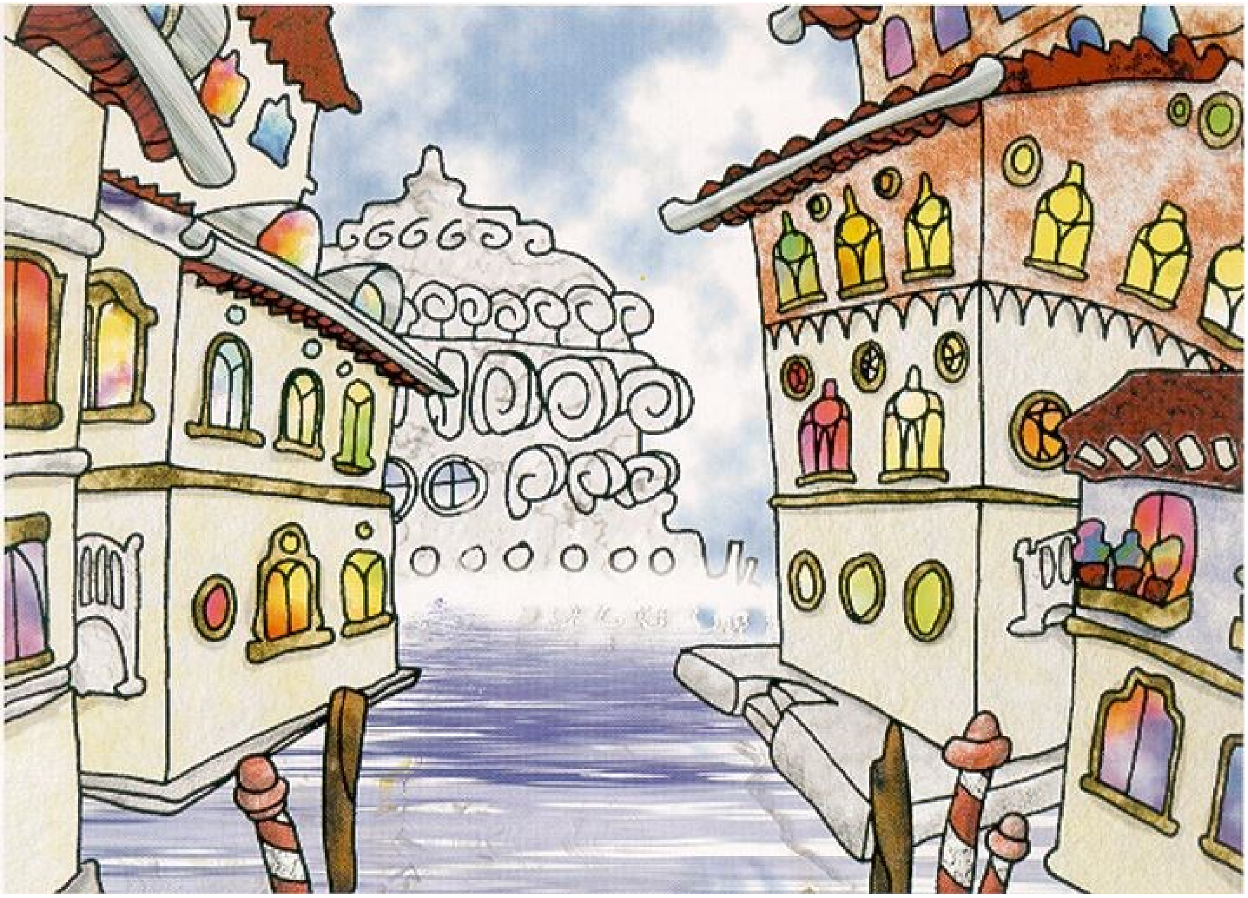
GREEN SCIENCES FOR SUSTAINABLE DEVELOPMENT FOUNDATION

The Summer School was an international initiative organized and managed by the new-born **Green Sciences for Sustainable Development (GSSD) Foundation** (www.gssd-foundation.org), a no-profit Foundation established in February 2020 and based in Venice.



The Foundation was constituted, pursuant to Article 14 and following of the Italian Civil Code, on February 17th, 2020.

The Foundation has legal personality since it was registered at the Prefecture of Venice on May 28th, 2020 as a non-profit organization. Any proceeds, annuities and profits deriving from the performance of the activities are used exclusively to pursue the purposes of the Foundation.

The Foundation is based in the Municipality of Venice. In order to pursue the statutory purposes, with the resolution of the Board of Directors, secondary offices, agencies and branches may also be established, also abroad.

The Foundation facilitates the participation in its activity of public bodies and administrations and private subjects, developing and increasing the necessary network of national and international relations functional to achieving its goals.

PURPOSES

Main aims of the Foundation are:

a) to encourage the development of scientific education and the dissemination of knowledge in the national and international fields of the sciences of a chemical, physical and environmental order and of the disciplines that care and promote sustainability with particular regard to Sustainable and Green Chemistry and their applications;

b) to support and disseminate scientific, technological and cultural development in Sustainable Development in accordance with the 17 Goals of the United Nations, in the sectors of the use of renewable resources, energy saving, intrinsically clean processes and products, with low or no environmental impact, not harmful to health and green remedies for climate change;

c) to promote initiatives supporting the transfer of research results, the protection of intellectual property and the birth of new entrepreneurship;

d) to promote the involvement and collaboration of public or private, local, national, EU, foreign or international subjects in pursuing the aims of the Foundation itself;

e) to promote the internationalization of teaching and research activities through the management of specific services and participation in joint initiatives with other subjects, public or private, national, EU or international.

ACTIVITIES

a) to organize and manage national and international Congresses and Conferences, education, specialization and updating courses and other advanced training activities such as Summer Schools, Forums and International Thematic Workshops, also in collaboration with other private and public institutions; the sub-Saharan African continent will be paid particular attention;

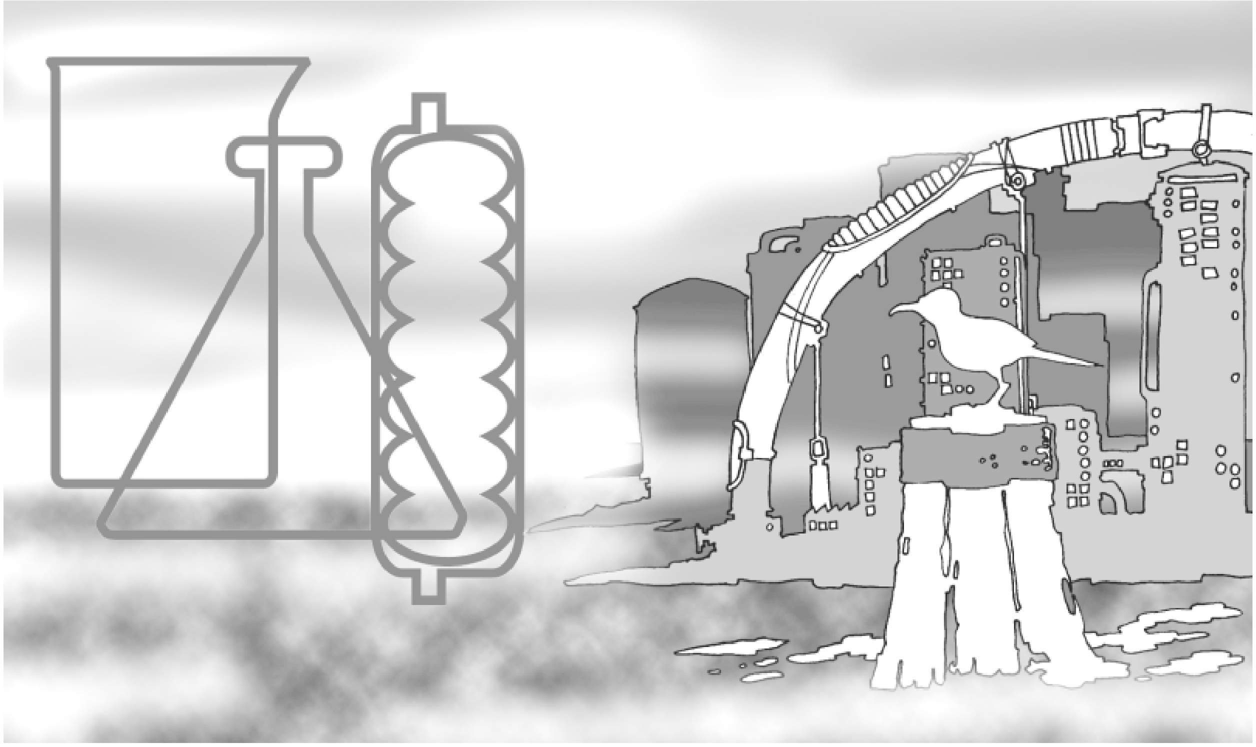
b) to publish books and magazines with their own ISBN;

c) to create and manage any laboratories or research centers also together with other public or private entities;

d) to participate in the operational management of scientific and/or technological structures of other foundations, structures and research bodies;

e) to enter into agreements, contracts, agreements or understandings with other subjects, public or private;

f) to promote and organize the collection of private and public funds and the request for local, national, European and international public and private contributions to be used for the purposes of the Foundation.



GREEN CHEMISTRY POSTGRADUATE SUMMER SCHOOL
6TH-10TH JULY 2020, ONLINE

BOOK OF ABSTRACTS

CONTENTS

WELCOME MESSAGE FROM THE CHAIR OF THE SUMMER SCHOOL

Dear Colleagues, dear Students,
It is with a great pleasure that I welcome you to the Postgraduate Summer School on Green Chemistry which for the first time is held by Remote. This Summer School has the scientific support of IUPAC, to which all Members of the Jury belong, and it is organized by the Green Sciences for Sustainable Development Foundation.
It is a great achievement that about half of the postgraduate students attending the School (about 200 in total) come from developing countries and have been awarded with a scholarship. So many grants were possible thanks to the participations of the Sponsors who believed in our organization: the Organization for the Prohibition of Chemical Weapons, PhosAgro, Ca' Foscari University, Kaimei Technology Co. Ltd. China, ICAS International and the Royal Society of Chemistry. Moreover, this Summer School has obtained the endorsement from UNESCO Roma, from Ministero dell'Ambiente, and from the City of Venice.
I would like to thank here all the teachers, and among them, I am very grateful to mention Jean-Marie Lehn and Michael Graetzel, with whom I had the honour to start my scientific career in Torino and Milano Universities and to work with on common interests' fields.
For different reasons I would like to thank Peter Licence, Aurelia Visa, Katalin Barta and Sergey Zinoviev and Fabio Aricò who were in different times students of the previous eleven editions of the Summer School in Venice.

The Summer School by Remote is of course more challenging than an event in person: while the students have the opportunity to be connected from everywhere, at the same time it is necessary to keep their attention high; this could be possible only with the engagement that we can reach with the scientific quality of the teachers. We hope to have gained the real participation of you Students to the Summer School activities by involving you in the discussion of the lectures and, not less important, through the poster sessions.
So, the programme is very rich and intensive and we hope to meet expectations of such a large number of students who have applied.

From the outcomes of this online Summer School we will learn on how to manage the next Summer Schools which will be held in person in Venice; the Green Sciences for Sustainable Development Foundation will surely support and follow the activities of this relevant initiative.

I would like to wish to all students a great success in their professional careers, with the hope that they will bring back to their Countries remarkable results in the field of Green Chemistry for Sustainable Development, as students from previous editions did.

Finally yet importantly, in this critical moment, the sustainable development is becoming every day a more crucial topic and we have to strongly believe in this: our motto is "Sustainability through Green Chemistry."

Pietro Tundo
Chairman of the Summer School

FOREWORD BY THE PRESIDENT OF IUPAC

It is a pleasure to welcome you all to the Green Chemistry Postgraduate Summer School in 2020 on behalf of IUPAC, the International Union of Pure and Applied Chemistry. IUPAC has had the pleasure and privilege to sponsor the Green Chemistry Summer Schools for many years, and there is a special connection through the IUPAC Interdivisional Committee on Green Chemistry for Sustainable Development, ICGCSD. A recent highlight was "IUPAC for Africa: Postgraduate Summer School on Green Chemistry", which took place in May 2019, last year, in Dar es Salaam, Tanzania, IUPAC's centenary year. This year, 2020, the novelty of the summer school is that it is taking place on-line, owing to the current worldwide health crisis. Besides the obvious difficulties, such a change also presents opportunities of involving participants in different ways exploiting modern information technology and social media for communication.

The world was already facing very important challenges of the environment and climate change, and how to achieve development in a sustainable way, reduce inequalities and move toward the sustainable development goals. Much of what underpins our way of life depends on products from chemical industry and on energy.

This summer school and its programme shows the way in which we can move forward to achieving these goals. It is an excellent opportunity for participants to learn not only about fundamentals and more about their research area, but also to gain a broader vision of the latest advances in green chemistry and chemistry as a whole and their importance in sustainable development. There is no doubt for me that it will become more important in the future. The shutdown that has been forced on us all by Covid-19 has shown how much we affect the environment. As we reset and begin our industrial and economic activities again, we must implement the lessons learnt and turn this situation into an opportunity to do things better.

Lectures by world experts on green chemistry and related areas, opportunities for questions and answers and interactive poster sessions mean that the summer school will certainly be a very rich experience for all participants, teachers and students alike. Finally, I would like to thank Professor Pietro Tundo and his team for organising this on-line summer school in challenging circumstances and which I am sure will be a success, leading to new ideas, future interactions, and collaborations in the area of green chemistry. I wish you all an excellent Summer School.

Christopher Brett
IUPAC President

SUMMER SCHOOL COMMITTEES

CHAIR OF THE SUMMER SCHOOL

- **Pietro Tundo,** *Chair of Interdivisional Committee of Green Chemistry for Sustainable Development and President of Green Sciences for Sustainable Development Foundation, Venice, Italy*

LOCAL ORGANIZING COMMITTEE

- **Fabio Aricò,** *Associated professor of Organic Chemistry, Ca' Foscari University of Venice, Italy*
- **Aurelia Visa,** *Romanian Academy "Coriolan Drăgulescu" Institute of Chemistry – Timisoara, Romania*
- **Elena Alfine,** *Green Sciences for Sustainable Development Foundation, Italy*
- **Emilia G. Pasta,** *Green Sciences for Sustainable Development Foundation, Italy*

WEB MANAGERS

- **Daniele Barzazzi**
- **Andrea Cester**
- **Enrico Siviero**
- **Fabrizio Romano,** *Ca' Foscari University of Venice*, Italy

ZOOM MANAGER

- **Paula de Waal,** *Mentat di De Waal P., Italy*

INTERNATIONAL SCIENTIFIC COMMITTEE (FROM IUPAC - ICGCSD)

- **Florent Allais,** *Directeur de l'URD Agro-Biotechnologies Industrielles (ABI) AgroParisTech*
- **Jane Wissinger,** *Environmental & Green Chemistry, Department of Chemistry, University of Minnesota*
- **Ana Aguiar Ricardo,** *Chemical & Biochemical Engineering, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa*
- **Aurelia Visa**, *Romanian Academy, "Coriolan Drăgulescu" Institute of Chemistry, Timisoara, Romania*
- **Klaus Kummerer,** *Leuphana University of Lüneburg. Institute for Sustainable and Environmental Chemistry, and International Sustainable Chemistry Collaborative Centre (ISC3), Lüneburg, Germany*
- **Buxing Han,** *Chinese Academy of Sciences, Beijing, China*
- **Jorge Colon,** *Chemistry Department, College of Natural Sciences, University of Porto Rico*
- **Nadia Kendile,** *Chemistry Department, Faculty of Women, Ain Shams University,Heliopolis, Cairo, Egypt*
- **Mester Zoltan,** *Department of Chemistry Queen's University Kingston, Ontario, Canada*
- **Liliana Mammino,** *University of Venda, Thohoyandou, South Africa*
- **Natalia P. Tarasova,** *Mendeleyev University of Chemical Technology, Moscow, Russia*

- **Konstantinos S. Triantafyllidis,** *Department of Chemistry Aristotle University of Thessaloniki, Greece*

INTERNATIONAL JURY FOR THE POSTER SESSIONS

- **Neil Coville**, *Chairman of the Jury and Emeritus professor of University of the Witwatersrand, Johannesburg, South Africa*
- **Ana Aguiar-Ricardo**, *Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal*
- **Mary Kirchhoff**, *Director of the ACS Green Chemistry Institute, Washington DC, United States*
- **Gloria Obuzor**, *Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria*
- **Aurelia Visa**, *Romanian Academy "Coriolan Drăgulescu" Institute of Chemistry – Timisoara, Romania*

LECTURES & TEACHERS
(alphabetical order)

FLORENT ALLAIS
Professor of Green Chemistry & Director, URD ABI – AgroParisTech, France
Biomass upgrading through the combination of Biotechnology, Green Chemistry and Downstream Process

PAUL ANASTAS
Teresa and H. John Heinz III Professor in the Practice of Chemistry for the Environment, United States
The Periodic Table of the Elements of Green and Sustainable Chemistry

FABIO ARICÒ
Associated professor of organic Chemistry, Ca' Foscari University of Venice, Italy
Bio-based platform chemicals and dialkyl carbonates: synthesis, functionalization and applications

KATALIN BARTA
Full Professor in Renewable resources and Organic Chemistry at the University of Graz, Austria
Cleave And Couple: Embracing Complexity In Renewable Resources

GAETANO CARMINATI
Senior Technical Expert from the National Authority for the Prohibition of Chemical Weapons, Rome, Italy
The role of the Italian National Authority

EMILIANO CAZZOLA
Cyclotron & Radiopharmacy Department Sacro Cuore- Don Calabria Hospital, Negrar, Verona, Italy
Green Radiochemistry: dream or reality?

JAMES CLARK
Professor of Chemistry at the University of York; Founding Director of the Green Chemistry Centre of Excellence and the Bio-renewables Development Centre, United Kingdom
Bio-based Solvents and their selection

MARCO EISSEN
Gymnasium Ganderkesee, Germany
Synthesis design with mass related metrics and health metrics

JONATHAN FORMAN
Science and Technology Advisor in the Global Security Technology and Policy Group under the National Security Directorate of Pacific Northwest National (PNNL), United States
Chemical Disarmament, Non-Proliferation, and Security
Is there a role for green and sustainable Chemistry?

MICHAEL GRAETZEL
Laboratory of Photonics and Interfaces, Ecole polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland
Energy Beyond Oil, Solar Cells that Mimic Natural Photosynthesis

BUXING HAN
Professor at Institute of Chemistry, Chinese Academy of Sciences (CAS); Academician of Chinese Academy of Sciences; Fellow of the Academy of Sciences for the Developing World (TWAS); Fellow of Royal Society of Chemistry; Director of CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics; Director of Shanghai Key Laboratory of Green Chemistry and Chemical Processes, P. R. China
Catalysis in Green Chemistry

MIRABBOS HOJAMBERDIEV
Uzbekistan-Japan Innovation Center of Youth, Tashkent 100095, Uzbekistan
Essential Retrospective Overview of IUPAC Projects on Sustainable Development Goals

PHILIP JESSOP
Canada Research Chair of Green Chemistry at Queen's University in Kingston, Canada Technical Director of GreenCentre, Canada
CO2-Switchable Materials

OLIVER KAPPE
Institute of Chemistry, University of Graz, Graz, Austria
Going with the Flow – The Use of Continuous Processing in Organic Synthesis

MARY KIRCHHOFF
Executive Vice President for Scientific Advancement Division at the American Chemical Society (ACS) and Director of the ACS Green Chemistry Institute, Washington DC, United States

KLAUS KUMMERER
Institute for Sustainable and Environmental Chemistry, and ISC Research and Education Hub, Leuphana University Lüneburg, Lüneburg, Germany
Design of chemicals and pharmaceuticals for environmental mineralisation

HAORAN LI
Professor at Department of Chemistry, Zhejiang University; Director of NHU R&D Center; Director of ZJU-NHU United R&D Center, P. R. China
Aerobic oxidation in vitamin industry

PETER LICENCE
School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, United Kingdom
Chemistry in-vacuo: Suck it and see!

ZHIMIN LIU
Institute of Chemistry, Chinese Academy of Sciences, 100190, Beijing, P. R. China
Ionic Liquids-Catalyzed Chemical Reactions

LILIANA MAMMINO
School of Mathematical and Natural Sciences, University of Venda, South Africa
The Study Of Molecules And The Design Of Substances:
Interfaces Between Green Chemistry And Computational Chemistry

MARIO MARCHIONNA
Corporate Head of Technology Innovation of Saipem, Italy
Hydrogen: the Missing Piece of the Zero-Carbon Puzzle?

KRZYSZTOF KRIS MATYJASZEWSKI
Department of Chemistry Carnegie Mellon University, Pittsburgh, United States
Towards Green Atom Transfer Radical Polymerization

GIUSEPPE MAZZITELLI
ENEA, Fusion and Nuclear Safety Department, Italy
An affordable and clean energy: nuclear fusion

MARTYN POLIAKOFF
The School of Chemistry, University of Nottingham, United Kingdom
Sustainability At The University Of Nottingham

NATALIA TARASOVA
Member of Governing Board of the International Science Council, Director of Institute of Chemistry and Problems of Sustainable Development, Mendeleev University of Chemical Technology of Russia and Chairholder of UNESCO in Green Chemistry for Sustainable Development, Russia
Green Chemistry within Planetary Boundaries

KONSTANTINOS S. TRIANTAFYLLIDIS
Professor, Department of Chemistry, Aristotle University of Thessaloniki, Greece
Adding value to biorefinery and pulp industry side-streams. Lignin valorization to fuels, chemicals and polymers

FERRUCCIO TRIFIRO’
Professor emeritus of the University of Bologna, Italy
The elimination of toxic reagents to realize a sustainable chemistry

FRANCESCO TROTTA
Associated professor of Industrial Chemistry University of Turin, Italy
Exploitation of renewable resources in Chemistry

PIETRO TUNDO
Emeritus Professor of Organic Chemistry Ca’ Foscari University of Venice, Italy
Reaction mechanism and energy profiles: how Green Chemistry complies with them. The case of Dimethyl Carbonate

JANE WISSINGER
Distinguished Teaching Professor of Chemistry and Organic Chemistry Laboratory Director at the University of Minnesota, United States
Green Chemistry Education: Pathway to a Sustainable Future

SERGEY ZINOVIEV
Senior International Cooperation Officer at OPCW, The Netherlands
Green Chemistry in the Context of the Chemical Weapons Convention, its Contribution to Chemical Safety and Security and the Peaceful Uses of Chemistry

Nobel Prize

JEAN-MARIE LEHN

Nobel Prize in 1987 in Chemistry for the synthesis of Cryptands: innovation in the field of supramolecular chemistry, France
Perspectives in Chemistry: Molecular – Supramolecular – Adaptive Chemistry

TIMETABLE

CEST – Central European Summer time

	MONDAY 6-July
9:00-10.15	OPENING CEREMONY
10.15-11:00	Michael Graetzel (Aurelia Visa)
11:00-11:45	Mario Marchionna (Aurelia Visa)
11:45-12:15	Q&A (Aurelia Visa)
12:15-12:45	Break
12:45-13:15	POSTER SESSION (N. Coville)
13:15-14:00	Giuseppe Mazzitelli (F. Aricò)
14:00-14:45	Emiliano Cazzola (F. Aricò)
14:45-15:30	Buxing Han (F. Aricò)
15:30-16:00	Q&A (F. Aricò)
16:00-16:30	Natalia Tarasova (N. Coville)
16:30-17:00	POSTER SESSION (N. Coville)

	TUESDAY 7-July
9:00-9:30	EuChemS - A. Aguiar-Ricardo ICGCSD - Buxing Han
9:30-10.15	Haoran Li (Buxing Han)
10.15-11:00	Pietro Tundo (Buxing Han)
11:00-11:30	Q&A (Buxing Han)
11:30-12:00	Break
12:00-13:00	POSTER SESSION (A. Aguiar-Ricardo)
13:00-13:45	Krzysztof Matyjaszewski (C. Brett)
13:45-14:30	Paul Anastas (C. Brett)
14:30-15:15	Alexander Sharabaiko (C. Brett)
15:15-16:00	Klaus Kümmerer (C. Brett)
16:00-16:30	Q&A (C. Brett)
16:30-17:00	Jane Wissinger (A. Aguiar-Ricardo)
17:00-17:30	POSTER SESSION (A. Aguiar-Ricardo)

	WEDNESDAY 8-July
9:00-9:30	ACS - Mary Kirchhoff Nottingham University - Martyn Poliakoff
9:30-10.15	Konstantinos Triantafyllidis (K. Barta)
10.15-11:00	Peter Licence (K. Barta)
11:00-11:45	Liu Zhimin (K. Barta)
11:45-12:15	Q&A (K. Barta)
12:15-12:45	Break
12:45-13:45	POSTER SESSION (Y. Chebude)
13:45-14:30	Philip Jessop (F. Allais)
14:30-15:15	Fabio Aricò (F. Allais)
15:15-16:00	Katalin Barta (F. Allais)
16:00-16:30	Q&A (F. Allais)
16:30-17:30	POSTER SESSION (M. Kirchhoff)

	THURSDAY 9-July
9:00-9:30	OPCW - Gaetano Carminati Ca' Foscari BAS - Alessandra Zorzi
9:30-10.15	Marco Eissen (A. Visa)
10.15-11:00	Francesco Trotta (A. Visa)
11:00-11:30	Q&A (A. Visa)
11:30-12:00	Break
12:00-13:00	POSTER SESSION (Gloria Obuzor)
13:00-13:45	Sergey Zinoviev (P. Jessop)
13:45-14:30	Jonathan Forman (P. Jessop)
14:45-15:30	Ferruccio Trifirò (P. Jessop)
15:30-16:00	Q&A (P. Jessop)
16:00-16:30	Mary Kirchhoff (J. Wissinger)
16:30-17:00	Liliana Mammino (J. Wissinger)

	FRIDAY 10-July
9:00-9:30	Società Chimica Italiana - Carmine Capacchione Marco Bella
9:30-10.15	Oliver Kappe (K. Triantafyllidis)
10.15-11:00	Florent Allais (K. Triantafyllidis)
11:00-11:45	James Clark (K. Triantafyllidis)
11:45-12:15	Q&A (K. Triantafyllidis)
12:15-12:45	Break
12:45-13:30	Jean-Marie LEHN (P. Tundo)
13:30-14:00	Q&A (P. Tundo)
14:00-17:00	CLOSING CEREMONY AND POSTER AWARDS

*(Moderators)

PROGRAMME

MONDAY 6 JULY MORNING

9:00-10.15 OPENING CEREMONY – Presenter: Pietro Tundo

1. ICGCSD and GSSD Foundation – **Pietro Tundo:** *Chair of the Summer School, Chair of Interdivisional Committee of Green Chemistry for Sustainable Development and President of Green Sciences for Sustainable Development Foundation, Venice, Italy*

2. Ca' Foscari – **Tiziana Lippiello:** *Vice Rector of Ca' Foscari University of Venice and Representative for International Relations, Venice, Italy*

3. IUPAC – **Christopher Brett:** *IUPAC President and Professor of Chemistry at University of Coimbra, Portugal*

4. International Council of Sciences - **Natalia Tarasova:** *Member of Governing Board of the International Science Council, Director of Institute of Chemistry and Problems of Sustainable Development, Mendeleev University of Chemical Technology of Russia and Chairholder of UNESCO in Green Chemistry for Sustainable Development, Russia*

5. PhosAgro – **Andrey Guryev:** *CEO of PhosAgro, Russia*

6. Chinese Chemical Society - **Zhigang Shuai:** *Vice President of Chinese Chemical Society, P. R. China*

7. Società Chimica Italiana – **Gaetano Guerra,** *President of Società Chimica Italiana, Italy*

8. Municipality of Venice – **Massimiliano De Martin:** *Councilor of the Municipality of Venice*, *Italy*

1st SESSION - Moderator: Aurelia Visa, *Romanian Academy "Coriolan Drăgulescu" Institute of Chemistry – Timisoara, Romania*

10.15-11:00 **Michael Graetzel,** *Laboratory of Photonics and Interfaces, Ecole polytechnique fédérale de Lausanne , Switzerland*
Energy Beyond Oil, Solar Cells that Mimic Natural Photosynthesis

11:00-11:45 **Mario Marchionna,** *Corporate Head of Technology Innovation of Saipem, Italy*
Hydrogen: the Missing Piece of the Zero-Carbon Puzzle?

11:45-12:15 Q&A

12:15-12:45 Break

12:45-13:15 **1st POSTER SESSION** - Moderator: Neil Coville, *Emeritus professor of University of the Witwatersrand, Johannesburg, South Africa*

MONDAY 6 JULY AFTERNOON

2nd SESSION - Moderator: Fabio Aricò, *Ca' Foscari University of Venice, Italy*

13:15-14:00 **Giuseppe Mazzitelli**, *ENEA, Fusion and Nuclear Safety Department, Italy*
An affordable and clean energy: nuclear fusion

14:00-14:45 **Emiliano Cazzola**, *Cyclotron & Radiopharmacy Department Sacro Cuore- Don Calabria Hospital, Negrar Verona, Italy*
Green Radiochemistry: dream or reality?

14:45-15:30 **Buxing Han**, *Professor at Institute of Chemistry, Chinese Academy of Sciences (CAS) P. R. China*
Catalysis in Green Chemistry

15:30-16:00 Q&A

3rd SESSION - Moderator: Neil Coville, *Emeritus professor of University of the Witwatersrand, Johannesburg, South Africa*

16:00-16:30 **Natalia Tarasova**, *Member of Governing Board of the International Science Council, Director of Institute of Chemistry and Problems of Sustainable Development, Mendeleev University of Chemical Technology of Russia and Chairholder of UNESCO in Green Chemistry for Sustainable Development, Russia*
Green Chemistry within Planetary Boundaries

16:30-17:00 **2nd POSTER SESSION** - Moderator: Neil Coville, *Emeritus professor of University of the Witwatersrand, Johannesburg, South Africa*

TUESDAY 7 JULY MORNING

9:00-9:30 SPONSORS and INSTITUTIONS

EuChemS - **Ana Aguiar-Ricardo**, *President of EuChemS Division on Green and Sustainable Chemistry, Portugal*

ICGCSD - **Buxing Han**, *Secretary of Interdivisional Committee of Green Chemistry for Sustainable Development, P. R. China*

4th SESSION - Moderator: Buxing Han, *Professor at Institute of Chemistry, Chinese Academy of Sciences (CAS), P. R. China*

9:30-10.15 **Haoran Li**, *Professor at Department of Chemistry, Zhejiang University; Director of NHU R&D Center; Director of ZJU-NHU United R&D Center, P. R. China*
Aerobic oxidation in vitamin industry

10.15-11:00 **Pietro Tundo,** *Chair of the Summer School, Chair of Interdivisional Committee of Green Chemistry for Sustainable Development, and President of Green Sciences for Sustainable Development Foundation*
Reaction mechanism and energy profiles: how Green Chemistry complies with them. The case of Dimethyl Carbonate

11:00-11:30 Q&A

11:30-12:00 Break

12:00-13:00 **3rd POSTER SESSION** - Moderator: Ana Aguiar-Ricardo, *Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal*

TUESDAY 7 JULY AFTERNOON

5th SESSION - Moderator: Christopher Brett, *IUPAC President and Professor of Chemistry at University of Coimbra, Portugal*

13:00-13:45 **Krzysztof Matyjaszewski**, *Department of Chemistry Carnegie Mellon University, Pittsburgh, United States*
Towards Green Atom Transfer Radical Polymerization

13:45-14:30 **Paul Anastas**, *Teresa and H. John Heinz III Professor in the Practice of Chemistry for the Environment, United States*
The Periodic Table of the Elements of Green and Sustainable Chemistry

14:30-15:15 **Aleksander Antonov**, *Head of department for international projects, PJSC PhosAgro, Russia*
Green Chemistry for Life

15:15-16:00 **Klaus Kümmerer**, *Institute for Sustainable and Environmental Chemistry, and ISC Research and Education Hub, Leuphana University Lüneburg, Lüneburg, Germany*

16:00-16:30 Q&A

6th SESSION - Moderator: Ana Aguiar-Ricardo, *Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal*

16:30-17:00 **Jane Wissinger**, *Distinguished Teaching Professor of Chemistry and Organic Chemistry Laboratory Director at the University of Minnesota, United States*
Green Chemistry Education: Pathway to a Sustainable Future

17:00-17:30 **4th POSTER SESSION** - Moderator: Ana Aguiar-Ricardo, *Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal*

WEDNESDAY 8 JULY MORNING

9:00-9:30 SPONSORS and INSTITUTIONS

ACS - **Mary Kirchhoff**, *Director of the ACS Green Chemistry Institute, Washington DC, United States*

Nottingham University - **Martyn Poliakoff**, *The School of Chemistry, University of Nottingham, United Kingdom*

7th SESSION - Moderator: Katalin Barta, *Full Professor at the University of Graz, Austria*

9:30-10:15 **Konstantinos Triantafyllidis**, *Professor at the Department of Chemistry, Aristotle University of Thessaloniki, Greece*
Adding value to biorefinery and pulp industry side-streams. Lignin valorization to fuels, chemicals and polymers

10:15-11:00 **Peter Licence***, School of Chemistry, University of Nottingham, Nottingham, United Kingdom*
Chemistry in-vacuo: Suck it and see!

11:00-11:45 **Zhimin Liu**, *Institute of Chemistry, Chinese Academy of Sciences, 100190, Beijing, P. R. China*
Ionic Liquids-Catalyzed Chemical Reactions

11:45-12:15 Q&A

12:15-12:45 Break

12:45-13:45 **5th POSTER SESSION** - Moderator: Neil Coville*, Emeritus professor of University of the Witwatersrand, Johannesburg, South Africa*

WEDNESDAY 8 AFTERNOON

8th SESSION - Moderator: Florent Allais, *Professor of Green Chemistry & Director, URD ABI – AgroParisTech, France*

13:45-14:30 **Philip Jessop**, *Canada Research Chair of Green Chemistry at Queen's University in Kingston, Canada, and Technical Director of GreenCentre, Canada*
CO2-Switchable Materials

14:30-15:15 **Fabio Aricò**, *Associated professor of organic Chemistry, Ca' Foscari University of Venice, Italy*
Bio-based platform chemicals and dialkyl carbonates: synthesis, functionalization and applications

15:15-16:00 **Katalin Barta**, *Full Professor in Renewable resources and Organic chemistry at the University of Graz, Austria*
Cleave And Couple: Embracing Complexity In Renewable Resources

16:00-16:30 Q&A

16:30-17:30 **6th POSTER SESSION** - Moderator: Mary Kirchhoff, *Director of the ACS Green Chemistry Institute, Washington DC, United States*

THURSDAY 9 JULY MORNING

9:00-9:30 SPONSORS and INSTUTUTIONS

OPCW - **Gaetano Carminati***, Senior Technical Expert from the National Authority for the Prohibition of Chemical Weapons, Rome, Italy*

Ca' Foscari BAS - **Alessandra Zorzi**, *Director of Ca' Foscari Library of Scientific Area, Venice, Italy*

9th SESSION - Moderator: Aurelia Visa*, Romanian Academy "Coriolan Drăgulescu" Institute of Chemistry – Timisoara, Romania*

9:30-10.15 **Marco Eissen** *Gymnasium Ganderkesee, Germany*
Synthesis design with mass related metrics and health metrics

10.15-11:00 **Francesco Trotta**, *Associated professor of Industrial Chemistry University of Turin, Italy*
Exploitation of renewable resources in Chemistry

11:00-11:30 Q&A

11:30-12:00 Break

12:00-13:00 **7th POSTER SESSION** - Moderator: Gloria Obuzor, *Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria*

THURSDAY 9 AFTERNOON

10th SESSION - Moderator: Philip Jessop, *Canada Research Chair of Green Chemistry at Queen's University in Kingston and Technical Director of GreenCentre, Canada*

13:00-13:45 **Sergey Zinoviev**, *Senior International Cooperation Officer at OPCW, The Netherlands*
Green Chemistry in the Context of the Chemical Weapons Convention, its Contribution to Chemical Safety and Security and the Peaceful Uses of Chemistry

13:45-14:30 **Jonathan Forman**, *Science and Technology Advisor in the Global Security Technology and Policy Group under the National Security Directorate of Pacific Northwest National (PNNL), USA*
Chemical Disarmament, Non-Proliferation, and Security. Is there a role for green and sustainable Chemistry?

14:45-15:30 **Ferruccio Trifirò***, Emeritus Professor of the University of Bologna, Italy*
The elimination of toxic reagents to realize a sustainable chemistry

15:30-16:00 Q&A

11th SESSION- Moderator: Jane Wissinger, *Distinguished Teaching Professor of Chemistry and Organic Chemistry Laboratory Director at the University of Minnesota*

16:00-16:30 **Mary Kirchhoff**, *Director of the ACS Green Chemistry Institute, Washington DC, USA*

16:30-17:00 **Liliana Mammino**, *School of Mathematical and Natural Sciences, University of Venda, South Africa*
The Study Of Molecules And The Design Of Substances: Interfaces Between Green Chemistry And Computational Chemist

17:00-17.20 IYCN - **Fun Man Fung***, elected Secretary of the International Younger Chemists Network, Singapore*

FRIDAY 10 MORNING

9:00-9:30 SPONSORS and INSTUTUTIONS

Società Chimica Italiana – **Carmine Capacchione**, *Member of Società Chimica Italiana, Italy*

Marco Bella – *Professor of Organic Chemistry at La Sapienza University of Rome and Member of Parliament of the Italian Republic in the Chamber of Deputies, Italy*

12th SESSION - Moderator: Konstantinos Triantafyllidis, *Professor at the Department of Chemistry, Aristotle University of Thessaloniki, Greece*

9:30-10.15 **Oliver Kappe**, *Institute of Chemistry, University of Graz, Graz, Austria*
Going with the Flow – The Use of Continuous Processing in Organic Synthesis

10.15-11:00 **Florent Allais**, *Professor of Green Chemistry & Director, URD ABI – AgroParisTech, France*
Biomass upgrading through the combination of Biotechnology, Green Chemistry and Downstream Process

11:00-11:45 **James Clark**, *Professor of Chemistry at the University of York; Founding Director of the Green Chemistry Centre of Excellence and the Bio-renewables Development Centre, United Kingdom*
Bio-based Solvents and their selection

11:45-12:15 Q&A

12:15-12:45 Break

FRIDAY 10 AFTERNOON

13rd SESSION - Moderator: Pietro Tundo, *Chair of the Summer School, Venice Italy*

12:45-13:30 **Jean-Marie LEHN**, *Nobel Prize in 1987 in Chemistry for the synthesis of Cryptands: innovation in the field of supramolecular chemistry, France*
Perspectives in Chemistry: Molecular – Supramolecular – Adaptive Chemistry

13:30-14:00 Q&A

14:00-15:00 **Poster Winners Awards** – Chairmen: Pietro Tundo, *Chair of the Summer School and Emeritus Professor of Ca' Foscari University of Venice*, *Italy* and Neil Coville, *Emeritus professor of University of the Witwatersrand, Johannesburg, South Africa*.

15:00-16:00 Closing Ceremony

1. **Chris Brett**, *IUPAC President, Portugal*
2. **Ana Aguiar-Ricardo**, *President of EuChems Division on Green Chemistry, Portugal*
3. **Fabio Aricò**, **Aurelia Visa**, **Paula De Waal** and **Elena Alfine:** *the Organizing Committee*

Closing Remarks and Group Photo

Pietro Tundo, *Chair of the Summer School, Venice Italy*

SUMMER SCHOOL TOPICS

1. Exploitation of renewable resources
2. New reaction pathways
3. Energy saving
4. Food safety
5. Climate Change damages mitigation
6. Education

TEACHERS’ LECTURE ABSTRACTS

FLORENT ALLAIS

Professor of Green Chemistry & Director, URD ABI – AgroParisTech, France

BIOMASS UPGRADING THROUGH THE COMBINATION OF BIOTECHNOLOGY, GREEN CHEMISTRY & DOWNSTREAM PROCESS

Under the patronage of local communities (Conseil Régional Grand Est, Conseil Départemental de la Marne and Grand Reims), AgroParisTech has built the team "Industrial Agro-Biotechnologies" (URD ABI) devoted to the **valorization of biomass.**

To carry out its missions, URD ABI has built, **from October 2012, a multi-disciplinary team. With expertise in chemistry, microbiology, process and chemical engineering as well as analytical chemistry, URD ABI is able to conduct fundamental as well as applied multi-disciplinary research projects**.

Our ambition is to develop and optimize **sustainable industrial processes and high valued-added products from agro-resources** (e.g., biorefineries by-products, agro-waste). More precisely, the scientists aim at the development of **platform molecules from biomass** that will be used to develop **new functional bio-based additives, polymers or materials, but also valuable sustainable fine chemicals**.

Our strategy is based on the combination of different approaches such as:

- Identifying a promising biobased synthon and develop new (macro)molecules with innovative properties

- Devising a safer, cheaper, greener and biobased alternative to a known commercial compound

- Working with industrials to overcome their technological and/or scientific bottlenecks

Examples illustrating these approaches will be presented.

PAUL T. ANASTAS

Director of Photonics and Interfaces (LPI), Institute of Chemical Science and Engineering Faculty of Basic Science Ecole Polytechnique Federale de Lausanne, Switzerland

THE PERIODIC TABLE OF THE ELEMENTS OF GREEN AND SUSTAINABLE CHEMISTRY

The field of green chemistry has a more than twenty-five year history of invention and innovation of creating new materials, new products, new manufacturing processes that perform better and cost less while being sustainable and safe for humans and the environment. The range of products invented and improved by green chemistry touches virtually every industry sector from agriculture to energy to medicine to plastics to electronics. While the scientific brilliance that enables these discoveries and innovations are essential and necessary, they are not sufficient. In order for green chemistry to make positive impact on a scale and with the urgency necessary to address the greatest challenges of our time as enumerated in the United Nations Sustainable Development Goals, there will need to be a supporting structure. This structure is outlined in the Periodic Table of the Elements of Green and Sustainable Chemistry using the metaphor of the original Periodic Table first introduced 150 years ago, to present the enabling conceptual frameworks, metrics, legal/economic/policy drivers to advance and empower the transition to a more sustainable world.

FABIO ARICÒ

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BIO-BASED PLATFORM CHEMICALS AND DIALKYL CARBONATES: SYNTHESIS, FUNCTIONALIZATION AND APPLICATIONS

In the last twenty years biorefinery has gained exceptional attention prompted by the need of substituting petroleum-based compounds with renewable one so to establish a bio-based economically self-sustained industry. The US Department of Energy (DOE) has published a list of 15 target molecules starting from 300 original candidates, that were considered of special interest for biorefinery development.[1] These compounds have been selected by taking into consideration factors such as available processes, economics, industrial viability, size of markets and their possible employment as a platform for the production of derivatives.

Over the years, due to the considerable progress in biorefinery development, this list, as well as, the criteria used to identify bio-based products has been revised. Several new compounds substituted the ones that have not received a great research interest. However, among the original selected chemicals, D-sorbitol, together with 5-hydroxymethylfurfural (HMF) derivatives still occupies a top position in the list as they encompass all of the desired criteria for a bio-based platform compounds. In fact, these building blocks have found numerous applications in the synthesis of chemicals, materials and bio-based polymers.

In this perspective, it is herein reported our recent work on the reactivity and upgrading of D-sorbitol, and HMF with organic carbonates employed as green reagents and solvents. Several industrially appealing products have been achieved with potential applications as high boiling green solvents (i.e. dimethyl isosorbide), biofuels candidates (2,5-bis-alkoxymethylfurans - BAMF) and monomers for bio-polymers [2].

Keywords: Biorefinery; Green chemistry; Organic carbonates; Carbohydrates

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KATALIN BARTA

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CLEAVE AND COUPLE: EMBRACING COMPLEXITY IN RENEWABLE RESOURCES

In this contribution I will talk about harnessing the inherent complexity of renewable resources for the development of novel catalytic processes – specially focusing on the conversion of lignocellulosic biomass to a range of products.[1-2]

Since lignin valorization has been one of bottlenecks toward the efficient utilization of lignocellulose, we devoted great attention to lignin chemistry and I would like to summarize some of our developments in this field, especially regarding the production of well-defined aromatic building blocks by stabilization of reactive intermediates.[2-4] I will also discuss the possibility of finding shorter, more sustainable catalytic paths, though the "cleave and couple" strategy. While cleave denotes depolymerization, "couple" involves the development of novel, sustainable transformations for the formation of C-C and C-N bonds[2,5,6] in order to access a range of interesting products.

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GAETANO CARMINATI

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THE ROLE OF THE ITALIAN NATIONAL AUTHORITY

Since the enter into force of the Chemical Weapons Convention, CWC, Italy, as a State Party, through the Law no. 496, implemented the National Authority and the build-up of national organisation. Along 22 years of work, the Italian National Authority has provided a constant support to the Technical Secretariat of the Organisation for the Prohibition of Chemical Weapons, OPCW, in the of training of inspectors, during the Sirian and Lybian chemical disarmament process, but also in the promotion of peaceful uses of chemistry with seminar activities, summer schools and exchange programmes devoted to young chemists in chemical industrial site at worldwide level.

Since 2016, the CWC has been promoted in national universities and academic environments in order to encourage a wider working opportunity offer by the OPCW as well as the possibility to strengthen a better scientific knowledge and expertise on these topics.

EMILIANO CAZZOLA

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GREEN RADIOCHEMISTRY: DREAM OR REALITY ?

Radiopharmaceuticals are medicinal products based on radioactive isotopes [1]. Those molecules are unique in showing metabolic processes and identify diseases growth and localization. Those probes are fundamental to combine the morphological structure of disease, obtained with CT or MR technique, to the metabolic pictures of the process at the base of the disease obtained with the PET (Positron Emission Tomography). PET images are obtained collecting radiation emitted from isotopes, present inside the radiopharmaceuticals, after their interaction and after their selective localization on the target tissue (e.g. tumor cell). This technology gives the possibility to evaluate the in-vivo tumor cell metabolism or, in presence of specific receptor, the interaction between receptor and radiopharmaceuticals to locate the malignant cell and characterize it [2]. This technique requires nuclear reactions, and consequently nuclear waste is necessarily produced. In the last years more and more processes were focused to reduce waste and to allow more environment friendly and green radiopharmaceutical production processes. This focus became necessary, especially today when the PET technique continues to grow and becomes one of the frontline techniques for tumors diagnosis; of course, the needs of radiopharmaceuticals is growing proportionally. Studies on waste management are at the base of important improvements on radiopharmaceutical production to achieve the same goals, like long term stability, fast reactivity and water reaction media [3]. All these requirements are common to the study for developing new radiopharmaceuticals based on water solution, with a fast kinetic and long-term stability on physiological environment.

Keywords

Green radiochemistry, nuclear waste, green improvement.

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JAMES CLARK

Professor of Chemistry at the University of York; Founding Director of the Green Chemistry Centre of Excellence and the Bio-renewables Development Centre, United Kingdom

BIO-BASED SOLVENTS AND THEIR SELECTION

Solvents are fundamental to many industrial processes but the replacement of many traditional but hazardous solvents is one of the greatest challenges in modern chemistry.

Many common solvents are now known to present unacceptable levels of risk to the environment, workers and in some cases the general public. New chemicals legislation notably REACH is proving to be especially challenging with solvents including some dipolar aprotic amides being classified as substances of very high concern. We must assume that many of our workhorse solvents will not be available in the near future.

In this lecture I will critically review the alternative solvents that are available to replace toxic or otherwise unacceptable solvents. In particular I will look at the emergence of bio-based solvents and how they can fit into a greener solvent landscape as well as support the growing bio-economy movement.

My talk will include a study on a "sustainable solvent selection service" whereby solvent replacements are chosen in a rather more logical way than more familiar and serendipitous approaches. This relies on the importance of multi-parameter indicators of solvent polarities including those provided through the Kamlet-Taft solvatochromic parameters or Hansen solubility parameters.

Case studies will be used to help illustrate how a new bio-based solvent can emerge from initial design through to commercialisation, upscaling and multiple sector applications.

MARCO EISSEN

Gymnasium Ganderkesee, Germany

SYNTHESIS DESIGN WITH MASS RELATED METRICS AND HEALTH METRICS

The process mass intensity (PMI) and the environmental factor (E) are common metrics which determine the greenness of chemical syntheses. Their importance can be similar to that of a life cycle assessment. In the last one and a half decades at least seven tools have been developed [1] [2] for the determination of environmental metrics. One of them is *EATOS*[3] (Environmental Assessment Tool for Organic Syntheses), which is considered a "powerful tool".[4] Its application will be presented using an example. Determining qualitative aspects in synthesis design is another goal. One of these aspects is health. Different concepts exist concerning this aspect, and a new one, based on the so called *Stoffenmanager*[5] methodology, will be presented by means of a case study.

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JONATHAN FORMAN

Science and Technology Advisor in the Global Security Technology and Policy Group under the National Security Directorate of Pacific Northwest National (PNNL), United States

CHEMICAL DISARMAMENT, NON-PROLIFERATION, AND SECURITY IS THERE A ROLE FOR GREEN AND SUSTAINABLE CHEMISTRY?

Explosive, incendiary, and toxic properties of chemicals have been exploited for use as weapons throughout the history of warfare. A history that has also seen diplomatic efforts (both with and without success) to limit, control, and/or completely ban certain chemicals as weapons through international treaties and agreements. Within these agreements chemistry finds its way into the policy sphere, where it intersects with diplomatic efforts and legal obligations. This lecture will discuss chemicals of war and the international arms control and disarmament agreements and obligations that impact them. The presentation will explore how chemistry influences policy, and where policy considerations and chemistry both challenge and support one another. In the context of the Green Chemistry Postgraduate Summer School, students will be asked to consider if there is a role for green and sustainable chemistry in chemical disarmament and non-proliferation, and chemical security.

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ENERGY BEYOND OIL, SOLAR CELLS THAT MIMIC NATURAL PHOTOSYNTHESIS

Learning from the concepts used by green plants photosynthesis, we have developed mesoscopic photosystems affording efficient solar light harvesting and conversion to electricity and fuels [1-4]. Solar cells using dyes, semiconductor quantum dots or perovskite pigments [5] as light harvesters have emerged as credible contenders to conventional silicon cells photovoltaic devices. Separating light absorption from charge carrier transport dye sensitized mesoscopic solar cells (DSCs) were the first to use a three-dimensional nanocrystalline junction for solar electricity production [1]. The conversion efficiency for DSC's is currently 14-15 % and over 22.7 % for pervoskite pigments. DSCs are simple and relatively inexpensive to manufacture, and they possess unique practical advantages including flexibility and transparency. These features along with excellent long-term stability have fostered first commercial applications, the industrial production of DSC's attaining presently the multi-MW/year scale. The fundamentally new concepts have been applied to realize the solar generation of hydrogen from water by photo-electrochemical cells [6] as well as the combination of perovskite solar cells and tandem devices with silicon for water electrolysers [7,8]. Recently our research focuses on the development of photosystems that achieve the efficient conversion of CO_2 to ethylene and ethanol by sunlight [9]. The current research status of this field will be presented.

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CATALYSIS IN GREEN CHEMISTRY

It is known that most reaction processes need catalysts. Thus, catalysis plays a crucial role in green chemistry. Green catalysts should have some typical characteristics, such as high activity, selectivity, and stability, nontoxic, green preparation process using abundant feedstocks, good reusability. Carbon dioxide (CO_2) is the main greenhouse gas, and it is also a renewable, abundant, and cheap C_1 feedstock. Biomass is abundant renewable carbon resource. Use of biomass and CO_2 as carbon source to produce fuels and value-added chemicals is of great importance for the sustainable development of our society. In recent years, we are very interested in catalytic conversion biomass and CO_2. In this presentation, I would like to discuss some of the recent results in our group on design of green catalysts and their application in conversion of biomass and CO_2 into valuable chemicals and fuels [1-11].

Keywords: Green Catalysis, Transformation, Biomass, Carbon dioxide, Chemical, Fuel

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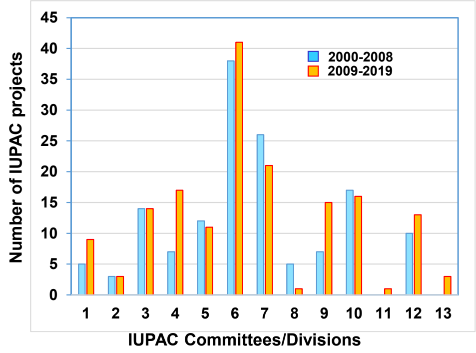
ESSENTIAL RETROSPECTIVE OVERVIEW OF IUPAC PROJECTS ON SUSTAINABLE DEVELOPMENT GOALS

The 17 Sustainable Development Goals (SDGs) are integrated and indivisible and balance the three dimensions of sustainable development: economy, society and environment [1]. Chemistry played a vital role in human civilization, and chemistry and chemical knowledge are equally important in today's modern society in tackling the global challenges and contributing to the achievement of SDGs. Since its formation, the IUPAC has been supporting various international projects addressing the goals listed in the IUPAC Strategic Plan. However, the contribution of the IUPAC Projects to sustainable development has not been fully assessed yet. Therefore, this preliminary study, as the first step, analyzes the IUPAC Projects carried out in the last 20 years against the SDGs [2] and identifies a long-lasting synergy between the IUPAC Projects and the SDGs. The total number of the preselected IUPAC projects is 309. Specifically, the preselected IUPAC Projects are classified (Figure 1) according to the Committees and Divisions of the IUPAC, reflecting their retrospective contribution to the achievement of SDGs. Note that the number of IUPAC Projects among the Divisions and Committees cannot be directly compared because of the difference in contents, years, and outcomes. Nevertheless, they constitute an important basis for future development. This study not only reflects the retrospective contribution of IUPAC Projects to the achievement of SDGs but also finds a synergy between the IUPAC Projects and demonstrates the IUPAC as a necessary, important, and valued contributor to the SDGs. This study increases the visibility of the IUPAC as a chemical knowledge-sharing international body in achieving the SDGs. The obtained data from this preliminary study shows that it is necessary to further investigate thoroughly the IUPAC Projects in collaboration with the representatives of the Committees and Divisions of the IUPAC: (i) to understand the contribution of IUPAC Projects in tackling local, regional, and global challenges by applying chemical knowledge, (ii) to comprehend the contribution of IUPAC Projects to the specific SDGs, (iii) to provide database to develop new research lines in green and sustainable chemistry, (iv) to develop knowledge/materials for teaching Green and Sustainable Chemistry, (v) to ensure the fullest possible weight of IUPAC view on Green and Sustainable Chemistry among other international organizations, (vi) to provide evidence and to advise the President and Executive Committee to develop Actions Plans on the successful achievement of SDGs, and (vii) to establish a cooperation with stakeholders for the achievement of SDGs.



DIVISIONS:

1: I - Physical and Biophysical Chemistry Division
2: II - Inorganic Chemistry Division
3: III - Organic and Biomolecular Chemistry Division
4: IV – Polymer Division
5: V - Analytical Chemistry Division
6: VI - Chemistry and the Environment Division
7: VII - Chemistry and Human Health Division

COMMITTEES:

8: Committee on Chemical Research Applied to World Needs (CHEMRAWN)
9: Committee on Chemistry and Industry
10: Committee on Chemistry Education
11: Committee on Publications and Cheminformatics Data Standards
12: Executive Committee
13: Interdivisional Committee on Green Chemistry for Sustainable Development (ICGCSD)

Figure 1. Classification of IUPAC Projects carried out in the years of 2000-2019 according to the Committees and Divisions of the IUPAC.

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CO_2-SWITCHABLE MATERIALS

Switchable materials are so common in our everyday lives that we rarely appreciate how green they are. We switch on the lights when we enter a room because we need the illumination, but we switch off the lights when we exit in order to save energy. The switchability of lights makes them greener and less energy-consuming than non-switchable lights would be. But should we not demand the same from our solvents, surfactants, drying agents, and coatings? A switchable solvent, one that dissolves a solute when needed and later releases the product when dissolution is no longer wanted, could make processes more efficient and less environmentally harmful. Switching the solvent "off" would precipitate the product without the solvent needing to be removed by energy-intensive distillation. Perhaps such a solvent could also be more easily recycled? Similar arguments can be made for the expectation that many switchable materials could be greener than their non-switchable predecessors. However, if the switchable material is highly toxic or the trigger used to switch the material causes pollution, then the technology will not benefit the environment at all.

This presentation will describe the advantages and disadvantages of several triggers for switchable materials, and then describe the chemistry and selected applications of CO_2-switchable materials. Examples of the widely varying problems that could be addressed by using CO_2 as a modifier include the following:

- nearly half of worldwide use of organic solvents is in paints and coatings, because water-based coatings are inferior.
- about 1/3 of the world's rubber crop is thrown away every year due to coagulation before processing, so that the environmental impact of the remaining natural rubber is increased by 50%
- 1/3 of the world population is suffering from fresh water shortages and yet industries are seeking more places to discard their wastewater.
- conversion of biomass into chemical products usually requires energy-intensive separation of the product from water. Could CO_2 be used to facilitate that separation?

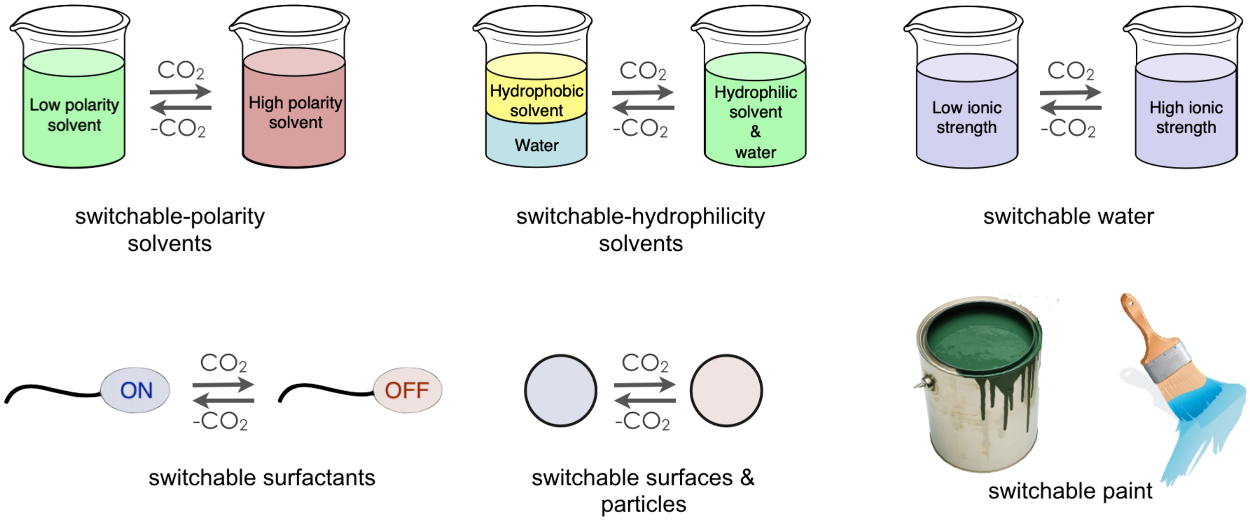

Figure 1. Some of the classes of CO2-switchable materials.

Keywords carbon dioxide; solvent; surfactant; surface; coatings

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GOING WITH THE FLOW – THE USE OF CONTINUOUS PROCESSING IN ORGANIC SYNTHESIS

Enhanced heat and mass transfer, precise residence time control, shorter process times, increased safety, reproducibility, better product quality and easy scalability are just a few of the advantages of flow chemistry and reason for the increasing implementation of continuous processes not only in academia but also into the fine chemical manufacturing sector. Notably, to make a process greener and more sustainable becomes eminently important when going from lab-scale to production scale. In this presentation, the question to which extent continuous flow processing has an impact as green technology, in particular on the synthesis of active pharmaceutical ingredients (APIs) on manufacturing scale, is discussed [1,2]. Based on the principles of both green chemistry and green engineering selected continuous processes are evaluated (Figure 1).

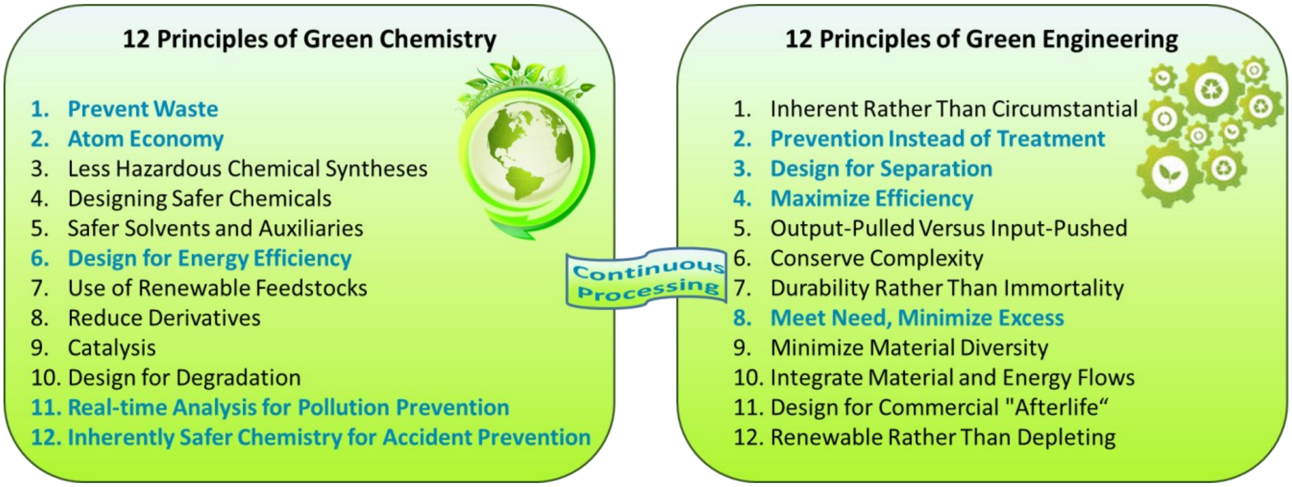

Figure 1. Twelve principles of green chemistry and green engineering and the impact of continuous processing highlighted in blue [2].

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DESIGN OF CHEMICALS AND PHARMACEUTICALS FOR ENVIRONMENTAL MINERALISATION

Pharmaceuticals and many chemicals are used in open applications such as personal care products, disinfectant, pesticides detergents or are released form products within their lifecycle into the aquatic environment. Such products and their constituents cannot be circulated within a circular economy (1). Only 20% or world's effluents are treated (2). However, even if there is treatment it does remove often a minor share of the water pollutants only. Furthermore, it has been found that advanced effluent treatment that is under discussion because of the limitations of conventional treatment can neither remove the majority of the pollutant. In contrast chemical treatment (e.g. advanced oxidation) often generates products of incomplete mineralisation (transformation products, TPs) that are most often unknown with respect to structure, fate and toxicity (3). It has been found however, that some are even more toxic than the parent compounds (4,5). Therefore, measures for input prevention at the source ("beginning of the pipe") are urgently needed (1). The molecules and their properties are at the very beginning of the pipe. Design for environmental degradation (green chemistry principle #10) addresses this. However, complete mineralisation has to be reached in the best case to avoid follow up-problems caused by unwanted products of incomplete mineralisation. In the presentation it will be demonstrated that this is feasible and how by applying several different methods for computational chemistry, analytical chemistry, toxicology and environmental microbiology (6-9).

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AEROBIC OXIDATION IN VITAMIN INDUSTRY

Keywords: aerobic oxidation, vitamin E, vitamin D3, catalysis, mechanism

Vitamins are essential compounds for life, which play an important role in metabolic function. The artificial synthesis of vitamins has been well developed during last few decades [1], among which the aerobic oxidation is an emerging and flourish field. Using O_2 as the oxidant, the aerobic oxidation is a potential green process with high E-factor, however, it is challenging to control the selectivity.

Herein, we introduce three applications of aerobic oxidation in vitamin industry (Figure 1), including the oxidation of beta-isophoron in petrochemical process for vitamin E production [2], the oxidation of 2,3,6-trimethylphenol in coal chemical process for vitamin E production [3-4], and the oxidation of acetyl-cholesterol in vitamin D3 production [5]. The development of green and efficient catalyst system will be focused, and we will show the progress of mechanistic study on these reactions.

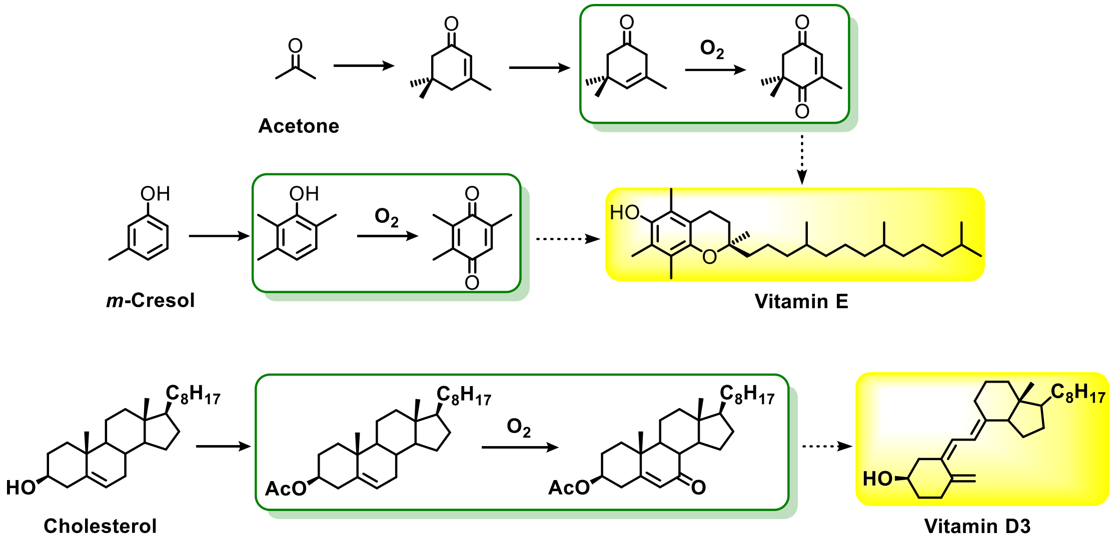

Figure 1. The brief industrial routes for production of vitamin E and vitamin D3.

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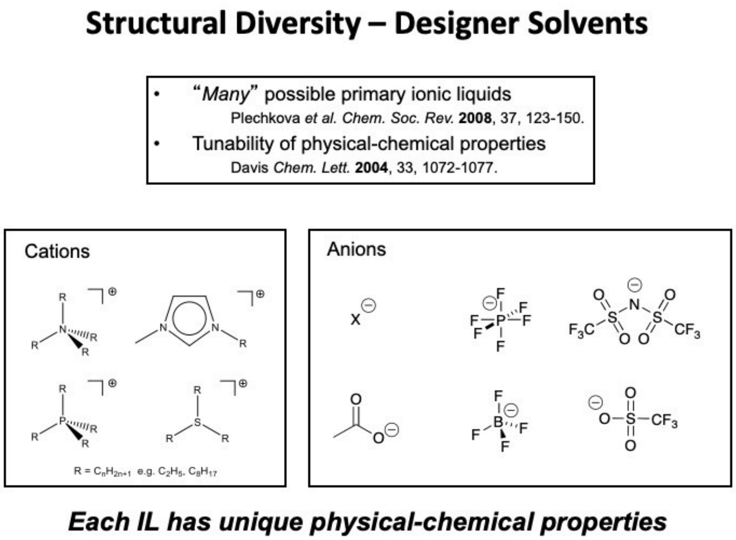
CHEMISTRY IN-VACUO: SUCK IT AND SEE!

Room Temperature Ionic Liquids are sterically hindered organic salts that exhibit melting points below the boiling point of water. Because they are composed entirely of ions, ionic liquids have almost zero vapour pressures and do not evaporate even under vacuum! This feature set alongside the large liquid-ranges observed for many ionic liquids has led to them being characterised as Green Solvents. Furthermore, structural diversity in the ionic components that can be brought together to form simple binary salts and mixtures, each with a unique set of physical and chemical properties, has led to them becoming known as designer solvents which could, in principle, be designed or engineered with a specific reaction of process in mind.

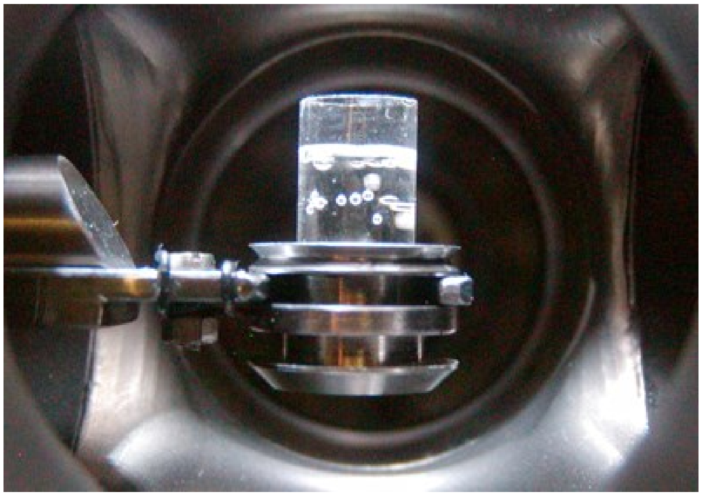

Structural Diversity – Designer Solvents

- *"Many"* possible primary ionic liquids
  Plechkova *et al. Chem. Soc. Rev.* **2008**, 37, 123-150.
- Tunability of physical-chemical properties
  Davis *Chem. Lett.* **2004**, 33, 1072-1077.

Each IL has unique physical-chemical properties

This lecture will give an overview of the basics physical chemistry that underpins the field of ionic liquids based chemistry, I will challenge the perception that these liquid solvents are indeed green and attempt to give examples where ionic liquid based technologies deliver advantages that may not be achieved using more traditional solvent systems.

I will explore opportunities to control chemistry via systematic ion choice and demonstrate the designer nature of simple systems to control physical parameters.
I will close with a brief overview of the impacts of science-based research across multiple scales, including a whole laboratory scenario.



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IONIC LIQUIDS-CATALYZED CHEMICAL REACTIONS

Around 70% chemical processes require for solvents, and ~20 million tons of harmful solvents are emitted to environment annually, resulting in harm to people and pollution to environment. Therefore, green solvents are highly required for green and sustainable development, which have attracted global attention. Ionic liquids (ILs) are organic melton salts at temperature below 100 °C, which are considered as a kind of green solvents because they have negligible vapor pressures. Moreover, they have unique properties such as wide liquid window, high thermal and chemical stability, wide electrochemical window and so on. Particularly, they can be designed with unique functions via choice of cations and anions, thus have wide applications in many areas. In chemical reactions, ILs can be used as the solvents and/or catalysts.

In this presentation, I will introduce the synthetic protocols and properties of ILs, followed by their applications in chemical reactions. Especially, I will present our recent work on IL-catalyzed chemical reactions [1-10]. A series of task-specific ILs that could absorb CO_2 chemically were designed, which realized the transformation of CO_2 with high efficiency under mild conditions [1-4]. For example, a CO_2-reactive protic ionic liquid (PIL), [$HDBU^+$][TFE^-], was synthesized by neutralization of a superbase 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with a weak proton donor trifluoroethanol (TFE). As a bifunctional catalyst for simultaneously activating CO_2 and the substrate, this PIL displayed excellent performance for catalysing the reactions of CO_2 with 2-aminobenzonitriles at atmospheric pressure and room temperature under metal-free conditions, producing a series of quinazoline-2,4(1H,3H)-diones in excellent yields. We constructed some IL-metal catalytic systems for CO_2 transformation, in which IL plays multiple roles: modifying the properties of the metal catalysts, activating CO_2 via forming intermediates, and activating substrates via H-bonding, and realized the transformation of CO_2 with high efficiency. For example, the combination of the IL [BMIm][BF_4] with Pd/C could catalyze the selective reduction of CO_2 with cyclic amines and H_2, producing formamides, methylamine, and 1,2-bis(N-heterocyclic)ethane, respectively, via changing reaction temperature. More recently, we discovered that the IL 1-butylsulfonate-3-methylimidazolium trifluoromethanesulfonate could catalyze ring-closing metathesis of aliphatic ethers to O-heterocycles via hydrogen-bonding under metal- and solvent-free conditions, affording a series of O-heterocycles including tetrahydrofurans, tetrahydropyrans, morpholines and dioxane in excellent yields (e.g., >99%) [10]. Our research work indicates that the ILs have promising applications in chemical reactions.

Keywords: Ionic liquids, chemical reaction, carbon dioxide, transformation, catalyst
Acknowledgements: The author thanks the National Natural Science Foundation of China (21890761) for the financial support.

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THE STUDY OF MOLECULES AND THE DESIGN OF SUBSTANCES: INTERFACES BETWEEN GREEN CHEMISTRY AND COMPUTATIONAL CHEMISTRY

The design of environmentally benign substances is part of the very definition of green chemistry. The design of new substances with specific properties relies on the knowledge of the properties of their molecules. In modern chemistry, the properties of molecules are mostly investigated with the approaches of theoretical/computational chemistry. This engenders extensive interfaces between the two areas, making cross-disciplinarity between green chemistry and computational chemistry important both in chemistry practice and at educational level [1, 2].

The lecture outlines the main concepts, approaches and capabilities of molecular design, and relates them to the principles and objectives of green chemistry, and to their predictable industrial relevance. The underlying pervasive perspective is the significance that specialists in the two areas come to “know each other” sufficiently well to be able to “talk to each other” professionally and work together for goals of common interest.

Keywords: design of environmentally benign substances, green chemistry education, molecular design, quantum chemistry methods, theoretical chemistry education.

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HYDROGEN: THE MISSING PIECE OF THE ZERO-CARBON PUZZLE?

Hydrogen is currently at the center of attention of public opinion as a new possible ‘pole star’ of a new energy future. The reasons for these great expectations can be ascribed to the fact that recourse to fossil fuels is one of the main causes of environmental pollution, at both global and local scale, whereas hydrogen (“which if burnt, produces only water”) is regarded as a solution to free us from fossil fuels and from the ‘carbon’ economy. Hydrogen is a typical energy carrier and a few hints will be given to their relevant features [1,2].

Hydrogen is currently used as an intermediate product in the chemical (mostly ammonia and methanol) and refining industries. It is produced mostly from Natural Gas in large scale plants using Steam Methane Reforming, a very mature technology. Hydrogen produced from Natural Gas has a high carbon footprint, considering that about 6-9 tons of CO_2 are co-produced (and emitted to the atmosphere) per ton of produced hydrogen, depending on Natural Gas composition. For this reason, Hydrogen produced from fossil fuels is nowadays named as “Grey” Hydrogen. The current production of Hydrogen is responsible of about 2.5% of CO_2 emissions worldwide.

For Hydrogen remaining in business, and then becoming a factor in the energy transition period and later, decarbonizing its production is a must. Partially decarbonized hydrogen produced from fossil fuels, through CO_2 Capture, is named “Blue” Hydrogen.

A completely different path is followed for the production of fully decarbonized, or “Green” Hydrogen. This path is already commercially available, though on a smaller scale than required for wide industrial application. It is the electrolysis of water, i.e. the use of electric power from renewable sources to break the water molecule into its constituent Hydrogen and Oxygen.

Starting from mostly publicly available information from other sources, we have recently tried to understand the factors affecting the role of decarbonized hydrogen in the energy transition, with specific focus on the 2030 scenario. The main factors considered are: Scale and cost of production, Current and future uses (industrial, residential, automotive) and Transportation and Storage aspects. Both Blue Hydrogen and Green Hydrogen have been considered.

In the presentation, the main qualitative conclusions of this investigation will be reported, a few of them here below in short synthesis:

- Both Green and Blue Hydrogen have the potential for gradually replacing Grey Hydrogen in current uses, to achieve decarbonization of the whole Hydrogen sector.
- The production of decarbonized steel will constitute the main new use for Green or Blue Hydrogen in the industrial sector, with large plants spreading from 2025 onwards.
- Blending of Hydrogen in existing large transmission pipelines is limited to a maximum of about 10% by volume. Replacing all compression stations, the limit may be extended to 20-30% depending on the specific material and operating conditions of the pipeline.
- As regards automotive uses, dedicated fleets of buses or trucks are the most promising options for early adoption.

Keywords: Energy carriers, hydrogen, electrolysis, decarbonization, energy transition

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GREEN MATERIALS BY ATOM TRANSFER RADICAL POLYMERIZATION UNDER BENIGN CONDITIONS

Fundamentals of copper-based ATRP (atom transfer radical polymerization) will be presented. Recently, by applying new initiating/catalytic systems, Cu level in ATRP was reduced to a few ppm. To combat unavoidable radical termination, several techniques for the regeneration of the catalytic systems have been developed. They include various benign chemical reagents such as ascorbic acid or sugars but also external stimuli: electrical current, light, mechanical forces and ultrasound. ATRP can be carried out without organic solvents, in bulk and in aqueous media under homogeneous conditions or in dispersed media. Reducing agent permit the reaction without deoxygenation in the flasks open to air. This is additionally aided by enzymatic degassing systems.

The range of monomers for ATRP has been expanded to (meth)acrylates and acrylamides from renewable resources. They have been used for synthesis of well-defined polymers with precisely controlled molecular architecture with designed shape, composition and functionality. Block, graft, star, hyperbranched, gradient and periodic copolymers, molecular brushes and various hybrid materials and bioconjugates were prepared with high precision. Some examples of nanostructured multifunctional hybrid materials for applications related to environment, energy and catalysis will be presented.

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AN AFFORDABLE AND CLEAN ENERGY: NUCLEAR FUSION

Nuclear fusion reactions are the energy source of the stars. Every second in the sun about 700 t of H are transformed into He. These reactions produce 4x10^{26} watts of which less than a billionth reaches the earth but it is sufficient to guarantee life on our planet.

To reproduce many small suns on earth would guarantee a source of clean, unlimited energy compatible with sustainable economic development.

The physical principles and the main problems that must be solved for the realization of the first nuclear fusion power plant will be illustrated.

After a brief review of the results obtained so far, the next steps will be shown.

In this decade three devices will start operating whose results will be fundamental for the design and construction of DEMO, the prototype of future power plants.

ITER, a big project, under construction in the south of France as result of an international collaboration, will begin operating after 2025 and will have to demonstrate the technical-scientific feasibility of fusion.

JT60-SA which will come into operation at the end of this year in Japan in collaboration with Europe that will study the advanced scenarios and finally DTT. DTT is an Italian project almost entirely financed by the Italian Government with an importatnt economic contribution of the EUROfusion European consortium which will come into operation in the second half of this decade. The main goal of DTT will be the study of power exhaust.

JULY 6-10, 2020 – ONLINE

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SUSTAINABILITY AT THE UNIVERSITY OF NOTTINGHAM

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This short presentation will complement the longer lecture by Pete Licence. It will outline three things (a) the role of sustainability and green chemistry in the undergraduate course at our University and how we linking Chemistry to the United Nations Sustainable Development Goals [1], (ii) our proposal of a Moore's Law for Chemistry, namely that over a given period, say five years, sustainable chemists should strive to reduce the amount of a chemical needed to produce a given effect by a factor of two and this process should be repeated for a number of cycles. (iii) our research project Photo-Electro which aims to transform chemical, a major new research programme in which we are partnering with the Universities of Bristol and Southampton with the aim of transforming how photochemistry and electrochemistry are used in the manufacture of chemicals developing new photo-reactors [3,4]. Photochemistry is potentially a very powerful tool for Green Chemistry not least because energy is delivered to reacting molecules far more selectively than by bulk heating. Indeed, more than a century ago, the pioneering Italian chemist, Ciamician, presented a very powerful vision of the where photochemistry could lead us [5]. Since then photochemistry has become a major strand of chemical research in academia. By comparison, its penetration into chemical manufacture remains comparatively modest because of a whole series of issues, mostly centred on the problems of carrying out large-scale photochemical reactions both efficiently and safely. Addressing these issues is one of the goals of Photo-Electro so that Ciamician's vision can be finally realized.

We thank the EPSRC, the Bill & Melinda Gates Foundation and the University of Nottingham for supporting our research

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GREEN CHEMISTRY WITHIN PLANETARY BOUNDARIES

Green chemistry may become an efficient tool for overcoming chemophobia and agrochemophobia as a variant of it. It is not a new, earlier unknown, trend. It is rather a compact formulation of thinking principles for well-trained and socially responsible chemists–scientists or technologists. The latter thesis is confirmed by the active practical application of green chemistry approaches in industry including in Russia. However, not only the business community, but also top-level politicians have begun to try to follow this way of thinking. The United Nations has pointed out that green chemistry is a key science development trend.

When increasing the productivity of crops, protecting them from pests, manufacturing new materials and products, developing transport, and creating medicines, humanity has caused unintended harm to the planet. In this connection, scientific papers devoted to the exhaustion of natural resources and the negative effect of human activity on the environment began to appear in the 1960s–1970s. According to some nonprofit organizations, such as the Global Footprint Network and the World Wildlife Fund, the consumption of natural resources for more than 40 years beginning from 1970 has exceeded the capability of our planet for their reproduction. This has led to a deficit in biocapacity, which is the capability of Earth's ecosystems to reproduce certain biomaterials and utilize the wastes of anthropogenic activity. According to the estimates of ecologists, in 2018, the needs of humanity exceeded the capabilities of nature by 1.5 times. In 2019, the Earth's annual resources were exhausted on July 29. Upon continuation of this trend, three planets like the Earth would be required to satisfy the needs of humanity by the year 2050.

A logical continuation of scientific knowledge accumulation is the concept of sustainable development, according to which economic and social development must be combined with the preservation of nature, i.e., the protection of the structure, functions, and diversity of the Earth's natural systems. The notion "planetary boundaries" has come into common use [1]. This field has actively been under development for the past ten years. Nine planetary boundaries, including climate change, loss of biodiversity, and change in terrestrial ecosystems have been described [2]. Numerical values were established for most boundaries. However, all the attempts to give quantitative estimates for the limits of the chemical pollution and aerosol content in the atmosphere have not yet given any results [3]. It has not been possible to calculate what amount of contaminants can lead to irreversible changes in the biosphere. Neither it was possible to determine the future of aerosols and their ultimate content safe for the planet in the atmosphere. This uncertainty, in our opinion, may be considered as one of the reason for the rise of chemophobia. Let us note that chemophobia, as well as any other phobia, cannot favor sustainable development. A cure for this disease is total chemical literacy formed beginning with one's school days and the responsible handling of chemicals, including their household use. The principles of green chemistry should become a code of conduct for specialists in chemistry who have graduated from institutions of higher education [4].

Keywords: planetary boundaries, chemophobia, green chemistry, chemical compounds, chemical literacy

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ADDING VALUE TO BIOREFINERY AND PULP INDUSTRY SIDE-STREAMS: LIGNIN VALORIZATION TO FUELS, CHEMICALS AND POLYMERS

Lignin is the most abundant natural aromatic/phenolic polymer and is one of the main structural components of lignocellulosic biomass, the other two being hemicellulose and cellulose. It is widely available in > 1 Mton annually in the form of lignosulphonate (mainly), kraft and soda sulphur-free lignins, as by-product of the pulp and paper industry. In the last twenty years, the intensive efforts of converting biomass to high added value fuels, chemicals and materials via the so-called "biorefinery" processes, such as the production of 2nd generation (cellulosic) bioethanol, has also led to the recovery of lignin streams, either as the remaining of acid/enzymatic hydrolysis of biomass carbohydrates or as initially isolated fraction via the organosolv and related "lignin-first" approaches. Despite the high potential of lignin as a low cost (waste / side-product) raw material for the liquid fuel and chemical industry, it is still under-utilized compared to the carbohydrate fractions of biomass, being mainly burnt to cover the heat and power needs of the main process, i.e. pulping, hydrolysis.

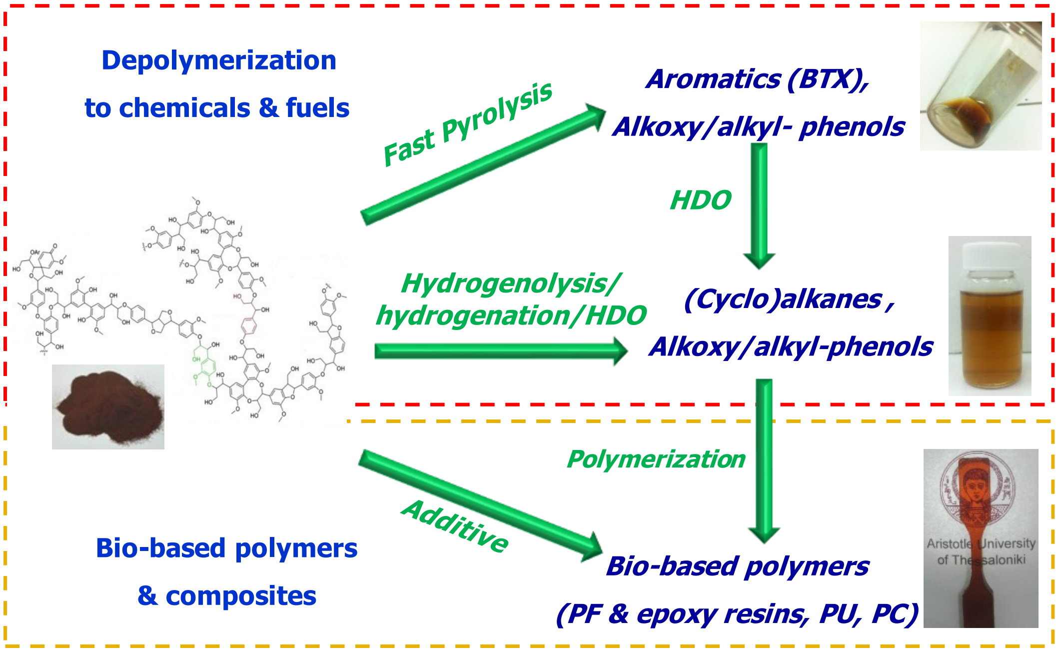

Fig. 1. Integrated approach employed for lignin valorization to fuels, chemicals and polymers

In this presentation, we will discuss the state of the art, as well as recent results of our group (Figure 1), on lignin production (biomass fractionation), characterization and valorization processes that are currently being developed and exhibit high exploitation potential. With regard to the down-stream processing, emphasis is placed on fast pyrolysis and hydrogenolysis of lignin which are capable to provide bio-oils that contain valuable phenolic and/or aromatic (BTX) compounds [1-5]. Such bio-oils can be hydrodeoxygenated (HDO) towards hydrocarbon fuels or can serve as source of monomers for the production of phenolic or epoxy resins or BTX based polymers. Due to the intrinsic functionality of lignin (surface hydroxyls) and its high aromaticity, it can also be utilized as reactive additive in epoxy or phenolic resins, without previous depolymerization to its monomer phenolic building units, thus reducing the need for petroleum-based monomers.

Keywords: lignocellulosic biomass; biorefinery; lignin; chemicals; biofuels; biopolymers

Acknowledgements

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THE ELIMINATION OF TOXIC REAGENTS TO REALIZE A SUSTAINABLE CHEMISTRY

The decrease in the use of benzene, of Cl_2 and HCN from the market would reduce the risk of catastrophic accidents in their production, their emissions in the environment and the risk of being used as chemical weapons by terrorists, or used by these to trigger accidents in chemical plants and to be used by governments in conflicts like in Syria. In this note I will refer essentially to the work I have done together with chemical companies in the past, with the objective to carry out processes without the use of highly toxic reagents avoiding the production of toxic by-products and co-products and therefore to realize a sustainable chemistry.

I have investigated the ammoxidation of propylene to acrylonitrile, the synthesis of adiponitrile by electrochemical dimerization of acrylonitrile produced from propane ammoxidation the oxidation of isobutane directly to methacrylic and the synthesis of aromatic nitrile by ammoxidation of alchyl-aromatics have been investigated as alternative to processes that uses HCN..The synthesis of propylene epoxide has been investigated by epoxidation with H_2O_2 or with by tert-butyl hydroperoxide The synthesis of ethylene fluoride has been realized through oxifluorination in alternative to the use ethylene chlorides as intermediate The synthesis of maleic anhydride has been realized by oxidation of n-butane as alternative to the use of benzene.

The synthesis of acrylonitrile from propylene has been realized with high yield as from propane with high yield with several new catalysts. The synthesis of maleic anhydrides from n-butane has been realized with $VO_2P_2O_7$ with different promoters and supports. The synthesis of aromatic nitriles has been realized with high yield with V-Ti and V/Sb mixed oxides as catalysts. The synthesis of propylene oxides has been realized with high yield with Tisilicalite as catalyst of epoxidation with H_2O_2 and molybdenum oxocomplexs as catalyst and tert-butyl hydroperoxide , The synthesis of methacrylic acid by oxidation of isubutane and the oxy fluorination of ethylene present till now low yield and cannot substitute process with high environmental impact.

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EXPLOITATION OF RENEWABLE RESOURCES IN CHEMISTRY

To face severe environmental and health concerns, limit greenhouse effects and improve the management of the foreseeable depletion of fossil resources, over the last decades, chemistry has moved towards the use of renewable resources for the production of energy and the synthesis of chemicals. Unlike materials deriving from fossils, which are often concentrated in a limited part of the world, renewable raw materials can be produced and utilized virtually everywhere. These renewable raw materials come from various value chains, such as vegetable oils, fats, cellulose, starch, wood and biomass. It is important to underline that, where possible, renewable raw materials coming from agricultural and forestry products should not be used for food or feed but expressly employed for the production of materials, heat, electricity or fuel. Today many products are made from renewable raw materials, which often require less energy consumption and use safer and eco-friendly synthetic routes. These include textiles, cosmetics, medicines, building materials, dyes, lubricants, intermediates and (bio)-polymers [1].

Of particular interest is the production of polymer materials using renewable resources. In fact, polymers have a wide range of applications and are of crucial importance in modern society. In 2015 a global production of 322 million tons of different polymers was recorded. However, only 1% is actually related to bio-polymers although a constant growth has been detected.

In this lesson I would like to share the results obtained over the last decades on the use of some starch derivatives i.e. cyclodextrins and linear dextrins to produce both cross-linked and branched polymers with an impressive number of applications [2]. Toxic solvent-free production and even solvent-free synthesis are possible, thus making these new materials particularly appealing.

Keywords: Raw materials, renewable resources, starch derivatives, dextrins, cyclodextrins

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REACTION MECHANISMS AND ENERGY PROFILES: HOW GREEN CHEMISTRY COMPLIES WITH THEM. THE CASE OF DIMETHYL CARBONATE

An important task for organic chemists toward a sustainable development is to discover and develop new reaction pathways in syntheses; they, coupled with metrics measurement, are the fundamental bases of green and sustainable chemistry.

Due to its benign nature, interest on Dimethyl Carbonate (DMC) has been enormously increasing in the last few decades: it is currently used in many chemical reactions as DMC can substitute chlorine-based chemistry. Green preparations of anti-inflammatory drugs, polymers, fragrances and solvents are widely reported. DMC peculiar reaction outcomes are based on its anisotropic electrophilic nature and because it follows exemplarily the Pearson's HSAB theory; in doing that, DMC and Dialkyl Carbonates (DACs) give unprecedent selectivity.

Comparison among Esters and Carbonates reaction pathways is dramatic in nucleophilic attach as it proceeds very differently: in methyl acetate the reactions take place almost exclusively at the carbonyl sp^2 because S_N2 substitutions on the methyl sp^3 have a higher activation energy; in the dimethyl carbonate, instead, the nucleophilic attach to the sp^2 carbon is more difficult, while the attach to the alkyl carbon is easier; the activation energy of the S_N2 reaction pathway is further decreased by entropic factors if formation of cycles is involved (Figure).

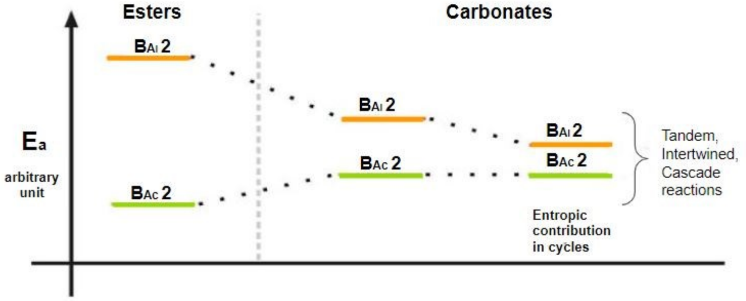

Figure. Activation energies in Esters and Carbonates; only $B_{Ac}2$ and $B_{Al}2$ reaction mechanisms are shown.
Ingold's terminology is adopted for esters and carbonates.

So, while in esters only sp^2 carbon is susceptible of a nucleophilic attack, in DACs Ea of $B_{Ac}2$ and $B_{Al}2$ are almost comparable; moreover, because the reagent is modified during the reaction, different reactions can take place in sequence in the same pot. Thus, tandem reaction, cascade, and intertwined reactions are possible in carbonates. This cannot occur in esters and wasn't ever reported.

S_N2 Nucleophilic substitution reactions at saturated and acylic carbons will be discussed; they take place either in basic and acidic-catalyzed conditions and allowed to get > 99% in *mono*-methylation reactions at the methylene carbon. Heterocycles of 5 and 6 atoms were obtained in quantitative yields, thus opening the way to novel compounds through a green chemistry pathway.

Limitations and new results will be presented: when the formation of cycles occurs, and when it doesn't. Moreover, also unimolecular substitutions take place.

Energy constraints and the dual electrophilic character of DACs originate unexpected reactivity and give results which are impossible for Esters.

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SPECTRUM OF GREEN CHEMISTRY EDUCATION: CHEMISTRY STUDENTS TO GLOBAL CITIZENS

This presentation will share how incorporation of green chemistry experiments into an introductory organic chemistry laboratory course over fifteen years ago at the University of Minnesota (U of MN), United States, has proliferated into many diverse and far-reaching educational programs. The topic of green chemistry immediately captured the interest of undergraduate students and graduate teaching assistants (TAs) who were inspired by green chemistry's "benign by design" approach to minimize environmental impact, reduce waste, and improve safety of chemical syntheses. This catalyzed research efforts to develop new green curriculum materials spearheaded by these students who could then see their efforts excite new classes of students in green chemistry practices. In a "pay it forward" paradigm, many of these students are now educators teaching green chemistry themselves in high school and college classrooms.

Along the way, green chemistry instruction at the U of MN has expanded from organic chemistry to those related to sustainable polymers, departmental safety initiatives, outreach programs, green engineering applications, and teacher workshops. Most notable is a senior level, dedicated, green chemistry course that includes a wide range of topics from sustainable nanomaterials to social justice and public health. This illustrates the multi-disciplinary nature of green chemistry and the ever-expanding connections which students come to understand is synonymous with a sustainable future. Specific examples of educational materials, including experiments modeling new innovations in environmentally-friendly plastics, will be presented as well as the positive feedback received from students of all career paths who valued learning about green chemistry's essential role in a healthy society and planet.

Keywords
green chemistry education, laboratory experiments, sustainable polymers

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GREEN CHEMISTRY IN THE CONTEXT OF THE CHEMICAL WEAPONS CONVENTION, ITS CONTRIBUTION TO CHEMICAL SAFETY AND SECURITY AND THE PEACEFUL USES OF CHEMISTRY

Article XI of the Chemical Weapons Convention provides for the international cooperation between States Parties in the areas of chemistry for peaceful purposes to stimulate the economic and technological development of chemistry. The rationale is to facilitating the right of States Parties to conduct scientific research, develop, store, produce and transfer chemicals for peaceful purposes. By doing so, the Convention offers tangible benefits in addition to restrictions and obligations. Within this mandate and as part of the vast portfolio of its international cooperation programmes, the Technical Secretariat of the OPCW looks into building capacity of institutions, facilitating good practices and offering education and training in some fields of chemistry. This work engages multiple stakeholders including research and academia, industry, National Authorities (NA) and other governmental entities.

Among such priority fields, which contribute to the OPCW mission of preventing re-emergence of chemical weapons and promoting safety, security and sustainability across the life chain of chemicals, there is green and sustainable chemistry. The latter, on one hand, provides concrete solutions for the replacement of potentially vulnerable processes or chemicals from the safety and security point of view. On the other, it nurtures the culture of sustainability and related professional ethics in the growing generations of chemists.

The OPCW has been supporting Green and Sustainable Chemistry for a number of years. The original focus was on related scientific research, mobility of researchers, education and dissemination of scientific information in the field. More recently in 2016, the Green Chemistry Initiative came into place which provided a forum for discussion among stakeholders on best practices of green and sustainable chemistry in providing solutions for safety and security and on the role of the OPCW in supporting such developments in cooperation with partners.

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PERSPECTIVES IN CHEMISTRY: MOLECULAR – SUPRAMOLECULAR – ADAPTIVE CHEMISTRY

Molecular chemistry has developed a wide range of very powerful procedures for mastering the organisation of matter and building ever more complex molecules from atoms linked by covalent bonds.

Supramolecular chemistry lies beyond molecular chemistry. It aims at constructing and implementing highly complex chemical systems from molecular components held together by non-covalent intermolecular forces. It relies on the development of pre-organized molecular receptors for effecting *molecular recognition*, catalysis and transport processes, on the basis of the *molecular information* stored in the covalent framework of the components and read out at the supramolecular level through specific interactional algorithms.

A further step consists in the design of systems undergoing *self-organization*, i.e. systems capable of spontaneously generating well-defined functional supramolecular architectures by self-assembly from their components, thus behaving as *programmed chemical systems*. Chemistry may therefore also be considered as an *information science*, the science of informed matter.

Supramolecular chemistry is intrinsically a *dynamic chemistry* in view of the lability of the interactions connecting the molecular components of a supramolecular entity and the resulting ability of supramolecular species to exchange their components. The same holds for molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibility, so as to allow a continuous change in constitution by reorganization and exchange of building blocks. These features define a *Constitutional Dynamic Chemistry* (CDC) covering both the molecular and supramolecular levels.

CDC introduces a paradigm shift with respect to constitutionally static chemistry. It takes advantage of dynamic diversity to allow variation and selection and operates on dynamic constitutional diversity in response to either internal or external factors to achieve *adaptation*.

The implementation of these concepts points to the emergence of *adaptive* and *evolutive chemistry.*

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STUDENTS' ABSTRACTS

The Abstracts are divided by topics and sorted in alphabetical order.

The Summer School Topics are the following:

1. Exploitation of renewable resources
2. New reaction pathways
3. Energy saving
4. Food safety
5. Climate Change damages mitigation
6. Education

The legend below explains the participants' contribution with their work to the Summer School: one star for those who sent their abstract, two stars for those who sent their abstract and poster, three stars for those who sent their abstract and poster and gave an oral presentation of their poster.

Those marked with four stars are the winners of the Poster Awards: six participants were selected by the Scientific Jury and gave an oral presentation on their work.

Legend:

★ Only Abstract

★★ Abstract and Poster

★★★ Abstract and Poster, presented during one of the Poster Scessions

★★★★ Abstract and Poster, presented during one of the Poster Scessions and Awarded during the Closing Ceremony

EXPLOITATION OF RENEWABLE RESOURCES

β-cyclodextrin nanosponges for the delivery of insulin
Silvia Lucia APPLETON

Hydroxyapatite as green biomaterial for sustainable water treatment
Sebastiano CAMPISI

Green synthesis of novel cyclodextrin-based polymers exploiting NADES
Claudio CECONE

Novel Fully Biobased poly (decamethylene -co-isosorbide-2,5-furandicarboxylate) Copolyesters with Superior Mechanical Properties and Enhanced Biodegradability
Yosra CHEBBI

Preservation of fresh-cut fruit with polyphenols and essential oils extracted with Microwave Assisted Extraction technique
Giulia COSTAMAGNA

Lipases And Cardoon: A Green Way To Obtain Bioplasticizers
Caterina DEGANUTTI

Pb(II) adsorption of Eco-friendly composite beads
Munkhbat DOLGORMAA

Breaking the limit of lignin monomer production *via* cleavage of interunit carbon-carbon linkages
Lin DONG

Cellulose dissolution by a new phosphonium-based deep eutectic solvent: a step towards industrial sugars production
Joy S. DOTSE

The use of Green solvent (Molten Hydrate Salt) in the one pot bioconversion of waste corn cob to succinic acid
Olayile EJEKWU

Modification of starch via the Biginelli multicomponent reaction
Eren ESEN

Bio-Inspired Facile Green Fabrication Of Gold Nanoparticles Using The Leaf Extract Of Combretum Sp., Its Antibacterial Evaluation And Biocompatibility
Olufunto Tolulope FANORO

Greener methods for lignin valorization: electrochemical upgrading of lignin monomers to valuable intermediates
Mahlet GAREDEW

Sustainable O-formylation of alcohols using CO2 as C1 building block
Gabriela GASTELU

Continuous flow tubular microreactor for the green synthesis of time-stable copper nanoparticles
Esteban GIORIA

Copper-catalyzed reductive functionalization of CO2 with amines: ligand effect on N-methylation and N-formylation
Hong-Ru LI

Producing Ethylbenzene from Lignin
Lingxiao LI

Recycling Agricultural Wastes and By-products in Organic Farming
Samar MOUSA

Efficient solvent-free transfer hydrogenation of bio-derived furfural to furfuryl alcohol by Pd(II) and Pt(II) complexes
Pamela. S. MOYO

Vanillin acrylate-based photocross-linked polymers
Aukse NAVARUCKIENE

Valorisation of Biomass to Furfuryl Alcohol
Novisi Komla OKLU

Candlenut Shell Lignocellulosic Valorization
Laurene PETITJEAN

ADMET polymers from sugars and castor oil
Marco PICCINI

Valorisation of CO2 in the cycloaddition to epoxides using MgO nanocatalysts
Cyprien POUCIN

Valorisation of waste biomass for sustainable development
Mitra SATAPATHY

Preparation of new bio-based acrylate monomers to produce sustainable polymers.
Raynold TECHIE-MENSON

Recycling and re-use of waste materials in households and agriculture
Thembani S. VUKEYA

Production of Benzene Polycarboxylic Acids from Organosolv Lignin by Alkali-Oxygen Oxidation
Yupeng WANG

NEW REACTION PATHWAYS

A Scalable Phase Transfer Catalyzed Synthesis of a BAY 43-9006 Precursor: from Batch Microwave to a Flow Packed Bed Reactor
Faith AKWI

Energy efficient solid-state metathesis reactions for nanocarbide synthesis
Rémi F. ANDRE

Mustard Carbonates: One-pot reactions to pharmaceutical intermediates
Mattia ANNATELLI

The (oligo)alkylation of oil fractions rich in aromatic hydrocarbons with C6-C10 – olefins in the presence of ionic liquids
Yetar Muzabbar BABASHOVA

Diffusion In Ionic Liquids - Aromatic Hydrocarbons Solutions By Molecular Dynamics Simulation
Maryna BAKUMENKO

Reversible phase behavior modulation of azobenzene ionic liquid-based emulsions by UV/vis irradiation
Doudou CAO

Mechanochemistry: Versatile and Functional Strategy for the Realization and the Recycling of Multi-Phase Materials
Roberta CAPUANO

New Efficient Preparation of Polyfunctionalized Furans by Solid Supported Systems
Elena CHIURCHIÙ

Reactivity of Ruthenium Acetylide Complexes Towards Carbon Dioxide
Silviu DOBROTA

Direct Synthesis of Diphenylamines from Phenols and Ammonium Formate Catalyzed by Palladium
Alejandra DOMINGUEZ-HUERTA

Investigating cyanogen rich Manihot esculenta efficacy for Ru phytomining and application in catalytic reactions
Sifelani DUBE

CoFe2O4-SiO2-SO3H magnetic nanocatalyst: An efficient catalyst for the synthesis of benzimidazoles and benzothiazoles
Mintu Maan DUTTA

Altering e-liquid composition and potential related hazards through the addition of water
Hanno C. ERYTHROPEL

Use POM anion-based ILs As High Performans Catalyst for Waste PET Alcoholysis
Pengtao FANG

Synthesis of NIPUs via thiol-ene polymerization of carbamates obtained from the Lossen rearrangement
Luca FILIPPI

Iron functionalised hydroxyapatites as efficient eco-friendly catalysts for air-quality protection
Melissa Greta GALLONI

Photodegradation of Textile Organic Dye waste using Biogenic Nitrogen-Phosphorous Codoped ZnO/CuO Nanocomposite
Mekdes GERAWORK

Transition-Metal-Free Synthesis of Benzo[c]chromenes via Visible Light
Micaela D. HEREDIA

A Novel Crystalline Azine-Linked 3D Covalent Organic Framework (COF) for CO2 Capture and Conversion
Xixi HOU

Unveiling the mechanism of pathway-tunable aliphatic carbonate synthesis from incorporated CO2 adducts by tracing oxygen isotopes
Xutao HU

Procognitive and antidepressant activity of novel anilide derivative with 5-HT1A/5-HT7 receptor antagonistic properties and PDE4/7 inhibitory activity
Agnieszka JANKOWSKA

Selective Hydrogenation of Fluoroaromatics using Rh Nanoparticles Immobilized on Functionalized Silica Supports
Souha KACEM

Searching for potential antibiotic adjuvants in the group of 5-(fluorobenzylidene)imidazolones
Aneta KACZOR

Amine-Responsive Disassembly of AuI–CuI Double Salts for Oxidative Carbonylation
Xingsi KANG

Critical mineral extraction and separation by intensified Solvent Extraction (SX), Ion Exchange (IX) and Molecular Recognition Technology (MRT)
Ali KHAZRAEI

Synthesizing Particular Metal Coordination Precursor for Nano Solid Electrolyte Preparation Toward to Its Unprecedented Bio-application to Inhibit the Biofilm Formation
Suneel LANKA

Fixation of CO2 into cyclic carbonates catalyzed by heterogeneous DBU based supported ionic liquid catalyst
Zhuo-Jian LI

Hypervalent Iodine reagents for Sulfonyl-transfer reactions
Diogo LOPES POEIRA

Inorganic-Perovskite Catalyzed Transfer Hydrogenation Reaction of Cinnamaldehyde Using Glycerol as a Hydrogen Donor
Tafadzwa P. MABATE

Catalytic hydrogenation of CO2 via porous-silica-supported Au nanoparticles in aqueous solutions
Siting NI

Understanding the mechanism of IrIII And PdII catalyzed CO2 hydrogenation in water
Edward OCANSEY

Highly Efficient Visible Light-Driven Rhenium Catalysis for CO2
Reduction through Second-Sphere-Modification Strategy
Li-Qi QIU

Reaction Pathways of Green Synthesis of SnO2 Nanoparticles by Chemical Precipitation Method towards Practical Application
Md. Wasikur RAHMAN

Cyclodextrin nanosponge formulations for the treatment of COVID-19
Azam REZAYAT

Eco-Friendly Ball Mill Synthesis of Cyclodextrin Crosslinked Biopolymers
Alberto RUBIN PEDRAZZO

Single Cu atom catalyst stabilized in metal oxide for CO_2 hydrogenation
Jianfei SUN

Reaction Density Functional Theory towards Green Chemistry
Weiqiang TANG

A more sustainable and highly practicable synthesis of aliphatic isocyanides
Kevin A. WAIBEL

Synthesis of Polyurea via polycondensation of Carbon Dioxide with Diamine Catalyzed by Base Catalyst
Peixuan WU

Enhancing electrochemical CO2 reduction to C2+ products via Copper-Cerium interface
Xupeng YAN

Synergistic catalysis of biological nonmetallic ionic liquid for glycolysis of waste polyethylene terephthalate
Haoyu YAO

Study on Cloud Point Pressure of [Emim][Tf2N] in Supercritical Carbon Dioxide Microemulsions Based on Non-ionic Surfactant and Role of Solubilized Water
Hongyue ZHU

Oxidation of Xiaolongtan lignite to oxygen-containing chemicals over $H_5PV_2Mo_{10}O_{40}$-H_2SO_4 by introducing methanol to suppress the formation of CO_2
He ZHUOSEN

ENERGY SAVING

High pressure switchable water: A path towards greener biomass conversion
Igor CUNHA

Developing Truly Green Solar Cells
Jayne ENGLISH

Synthesis and Characterization of TiO_2 Nanoparticles Prepared Using Natural Extract of Adansonia Digitata
A. FALL

Tailoring high-quality fuels with renewable biomass
Yaxuan JING

Structural evolution characteristics of Huolinhe lignite during heat treatment: Based on coal oxidation
He LI

Electrochemistry
Fang LIN

Bio-inspired of Fe doped $BiVO_4$ Nanoparticles via Hyphaene thebaica natural extract and their photocatalytic MB degradation properties
Hamza MOHAMED

Eco-friendly hybrid capacitor based on Ni/Al Layered Double Hydroxide and reduced Graphene Oxide composites
Elisa MUSELLA

Selective Oxidation of Methane
Hassan Javed NAGRA

Perovskite Catalyst for Heterogeneous Aerobic C-H Oxidation Reactions
Yeşim ŞAHİN

Effect of Ni NP morphology on catalyst performance in non-thermal plasma-assisted dry reforming of methane
Kristy STANLEY

Dual-Function Textile Supercapacitor: A New Green & Sustainable Energy Storage Device
Joana S. TEIXEIRA

Flexible Pressure Sensor Based on Silver/Graphene Nanocomposites Was Prepared By One Step
Zhi-Gang WANG

FOOD SAFETY

Comparative Study On The Environmental / Oral Health Effect Of Neem Twigs And Synthetic Toothbrush
Chiemena AMADI

Comparison of Extraction Technique on Hypoglycaemic Activity of Ethanolic Extract of Acacia arabica Plant
Neena ARORA

Characterization and Evaluation of In vitro α-glucosidase Inhibitory Property of Cacao (theobroma cacao) Pod Husks Extract: A Potential Source of Herbal Supplement
Venchie BADONG

Functionalized coated magnetic nanopartcicles for lead removal
Chimaine FEUDJIO TSAGUE

Synthesis and Characterization of New Molecularly Imprinted Polymers for Melatonin Delivery
Gjylije HOTI

Preconcentration of bisphenol S and bisphenol F from food samples using dummy molecularly imprinted polymer (DMIP)
Anna KUBIAK

Long-term stable infant formula – conceptual product design study
Fan-Hsuan LIU

Polysaccharide-derived materials for greener destruction of organophosphates
José Guilherme LOPES FERREIRA

The use of the biotechnology to resolve the contamination of soils and water
Mohamed MALDANI

The Complexation Of Oxyresveratrol In Cyclodextrin Based Nanosponges Complexes Enhances Bioactivities And Protection
Adrián MATENCIO

Facile removal of fluoride ions from water using triethylamine modified polyethylene adsorbent
Gerald W. MBUGUA

Surface modification of titanium oxide as a support of metal nanoparticles for solar driven water splitting to produce hydrogen
Peter MWANGI KIMANI

Effect Of Eucalyptus Oil On Reduction Of Bacterial Growth In Drinking Water
Jerome MWEMEZI

Testing the Inclusion Complexes of Oxyresveratrol and β-Cyclodextrin in Juice and Milk Food Models
Silvia NAVARRO-ORCAJADA

Phytochemical Screening and Antimicrobial Properties of the stem of Nuclea pobeguinii
Segun Festus ODEWALE

Production and formulation of an ecological mixed fertilizer based on rock phosphate and plant growth promoting bacteria
Imtinen SGHAIER

Adsorptive Removal Of Methylene Blue Dye Using A Novel Hybrid Polymer Hydrogel Containing Activated Carbon Or Tio2 Nanoparticles
Syed Sikandar SHAH

Nitrification Characteristics Of Nitrite To Nitrate For Nitrogen Removal And Nitrous Emission
Consolee SIBOSIKO

Contribution Of Tartaric Acid To The Free Radical Scavenging Activity Of Ascorbic Acid
Crina VICOL

CLIMATE CHANGE DAMAGES MITIGATION

Catalyst development for the conversion of renewable carbon sources and energy - overcoming the fossil-based economy
Anna Katharina BEINE

CO2 electroreduction: Enhanced activation and selectivity by ionic microhabitat
Jiaqi FENG

Design, synthesis and characterization of new PGM-based half-sandwich complexes for CO2 hydrogenation to formates and N,N-diethylformamide
Siphelele MALAZA

Development Of New Homogenous Catalysts For Co2 Reduction To Formates
Asanda C. MATSHEKU

Estimating net oxygen released by the restored mangrove forests in Southeast Asia
Cretus MTONGA

Sustainable Functional Constructs Engineered From Cellulose Nanofibers to Stifle Electromagnetic Pollution
Avinash R PAI

Uncontrolled waste disposal practices in low-income areas
Neani TSHILANDE

EDUCATION

Teaching Green Chemistry To Deaf Students: A Brazilian Case Study
Carlos Alberto DA SILVA JÚNIOR

1. EXPLOITATION OF RENEWABLE RESOURCES

β-cyclodextrin nanosponges for the delivery of insulin

★★★

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Abstract

Cyclodextrin-based nanosponges have recently gained great attention as drug delivery systems [1]. This can be certainly justified by their well-known outstanding properties: they are safe, readily available in nature, biodegradable, easy to produce and inexpensive and their synthesis is moving towards greener processes essential for a future scale up [2].

In this study nanosponges were investigated for the oral delivery of proteins, which is a scarcely explored field and, more in particular, insulin, indicated for the treatment of diabetes. The nanosponge formulation was developed using a top-down approach in order to obtain a stable nanosuspension, which was subsequently loaded with the protein of interest. A physicochemical characterization and *in-vitro* tests were performed.

The suspension was found to be stable (nanometric and with high negative zeta potential) and able to load insulin (about 14%). Its swelling influenced the *in-vitro* release kinetics of insulin, thus confirming its ability to release the drug gradually and in a pH-dependent manner particularly useful for oral administration. The cytotoxicity test (MTT) and the intestinal permeation test (Caco2 assay) revealed the lack of toxicity and suggested that this nanosponge plays a role in promoting the intestinal absorption of insulin.

The results collected up to now justify the continuation of this study to determine its effectiveness *in vivo*.

Keywords cyclodextrin-based nanosponges, insulin, oral delivery.

Acknowledgements

The authors are thankful to Roquette Frères (Lestrem, France) for their support.
The authors report no conflicts of interest.

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Hydroxyapatite as green biomaterial for sustainable water treatment

★★★

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Abstract

Hydroxyapatite (HAP) is a well-known biomaterial, widely used in biomedical field. The general chemical formula, $Ca_{10-x}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x}$ with $0<x<1$, encompasses both stoichiometric and no-stoichiometric solids. The variability of Ca/P ratio influences the acid/basic surface properties of HAPs[1], which are amphoteric solids exposing both acidic and basic groups at the surface. In addition, the high structural flexibility allows within certain limits to replace lattice ions with other cations or anions without any significant lattice distortion [1]. Doubtless, HAP is a complex material. However, far from being a limitation, this complexity makes HAP a multifunctional material with interesting surface properties exploitable for several applications, such as the removal of heavy metals in polluted wastewater. The metal trapping process on HAP proceeds through three mechanisms: ion exchange, surface complexation, dissolution-precipitation [2].

In this work synthetical HAP has been tested as adsorbent towards selected heavy metal ions (Pb^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Cr^{6+}). The adsorption capacity and relative affinity of metal ions for HAP were evaluated by adsorption tests, carried out in batch mode with single- and multi-metal solutions. Microcalorimetric titrations, modelling of adsorption volumetric isotherms and characterization of HAP and Me/HAP materials allowed to gain knowledge on the thermochemistry and mechanisms of metal uptake on HAP. Depending on the nature of the metal ion, different mechanisms were active The immobilisation of Pb^{2+}, Cr^{3+} and Cd^{2+} on HAP occurred through exothermal surface precipitation or dissolution/precipitation mechanism. This was evident in the case of Pb^{2+}, for which the formation of a new crystalline phase $Pb_{10}(PO_4)_6(OH)_2$, hydroxypyromorphite, as detected by X-Ray Powder Diffraction (XRPD) and transmission electron micrographs with energy-dispersive X-ray analysis(TEM-EDX), confirmed the occurrence of a dissolution/precipitation mechanism. The immobilization of small bivalent cations (Cu^{2+}, Co^{2+}, Ni^{2+})[3] did not imply the formation of new crystal phases, but rather a surface complexation mechanism seems to be responsible for their immobilization on HAP. It is then possible to address the metal ion uptake taking advantage from the different binding affinity of HAP surface groups towards distinct metal ions. Unfortunately, highly harmful Cr^{6+} species are not trapped on HAP, being Cr^{6+}prevalently present in water as oxo-anions having limited interactions with HAP surface. Conversely, HAP showed a remarkable affinity towards Cr^{3+} [4], that is the main product of Cr^{6+} reduction. We then proposed the heterogenization of chemical reduction process of Cr^{6+} in combination with an adsorption process of the formed Cr^{3+} species, by using a novel material (Sn/HAP), which consists in hydroxyapatite functionalized with Sn^{2+} to synergistically combine the reducing properties of Sn^{2+} species with the adsorption capacity of HAP. Characterization analyses by TEM-EDX and X-ray photoelectron spectroscopy (XPS) proved the occurrence of the heterogeneous reduction and immobilization phenomena at the interphase.

Definitively, HAP is a highly versatile and ecofriendly material that can be properly synthesized or modified to enable the selective removal of heavy metal ions from polluted wastewaters.

Keywords water remediation**;** hydroxyapatite**;** interphase phenomena;

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Green synthesis of novel cyclodextrin-based polymers exploiting NADES

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Abstract

Designing chemicals and processes to reduce or eliminate the use and generation of hazardous substances is one of the main aims of Green Chemistry. Besides, since solvents are present in most of industrial processes and comprise almost 60% of all industrial emissions, they represent one of the most active area of research [1]. Recently, a sustainable alternative to petroleum-based solvents has been given by deep eutectic solvents (DES), which consist of a mixture of organic compounds characterized by a lower melting point in respect to the individual components. Through the formation of hydrogen bonds DES components, associate with each other, forming a eutectic mixture [2]. Among others, natural low-cost compounds such as sugars, carboxylic acids, alcohols and amino acids have been applied for the formation of the so called natural deep eutectic solvents (NADES). In particular, the exploitation of choline chloride and citric acid systems have been extensively studied and reported [3].

βCD-based polymers are a class of materials widely studied for pharma, food, and environmental applications, thanks to their features in the controlled release of drugs and absorption of undesired substances. However, most of the synthesis report the use of organic solvents or toxic reactants, hence, describing a green way to obtain such class of materials would offer great benefit to the process [4]. In this work, the synthesis of a βCD-based polymer has been reported using a NADES composed of citric acid and choline chloride.

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Novel Fully Biobased poly (decamethylene -co-isosorbide-2,5-furandicarboxylate) Copolyesters with Superior Mechanical Properties and Enhanced Biodegradability

★★★

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Abstract

This work spotlighted a successful synthesis of a novel series of fully biobased poly(decamethylene-co-isosorbide 2,5-furandicarboxylate)s (PDIsFs) copolyesters from dimethylfuran-2,5-dicarboxylate (DMFD), 1,10-decanediol (1,10-DD) and isosorbide (Is) by melt polycondensation, using titanium(IV) isopropoxide catalyst. The chemical structure and composition of the resulting polymers were confirmed by ^{1}H NMR and FTIR spectroscopies. Satisfactory weight-average molecular weights (Mw) in the 55,300-84,500 g/mol range and random microstructures were found for PDIsFs. Results showed that Is unit incorporation into the copolymers molecular chains was dramatically effective in increasing the glass transition temperatures (Tg) and in delaying the degradation temperature at 5% weight loss ($T_{d,5\%}$) of PDIsFs. Hence, an excellent improvement of the thermal stability exceeding 405 °C for all copolyesters was obtained. In addition, the mechanical properties as well as the degradation behavior in soil of PDIsFs materials were duly investigated in detail. The biodegradation rate of the prepared copolyesters depended on the comonomer ratio. Rotational rheometry characterization of polymer melts revealed prevailing viscous properties for all formulations, whereas the presence of Is diol favored a Newtonian behavior. Oxygen induction time (OIT) measurements by chemiluminescence (CL) revealed that isosorbide incorporation also dramatically increases polyester thermo-oxidative stability. Taking advantage of their features, PDIsFs have the potential to serve as innovative and promising biobased polymers for practical applications such as sustainable and ecofriendly plastic packaging.

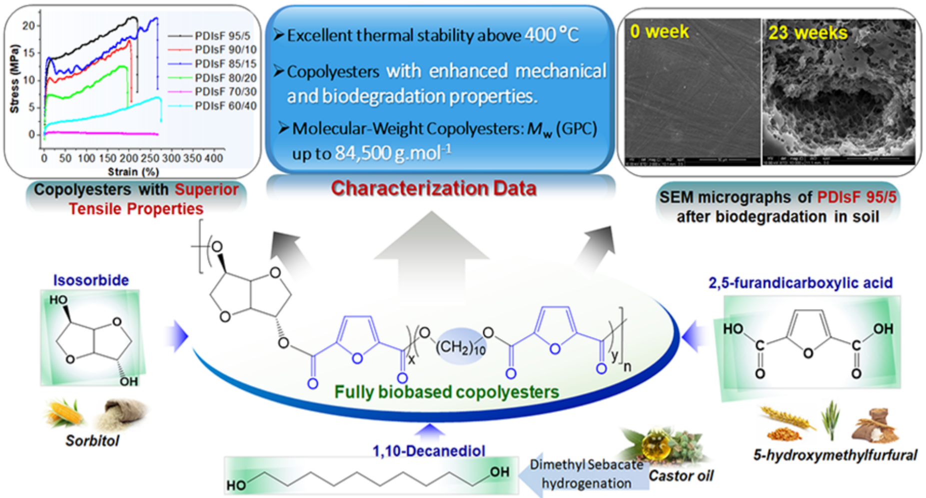

Figure 1. Synthesis and characterization of new fully biobased Poly(decamethylene-co-isosorbide 2,5-furandicarboxylate)

Preservation of fresh-cut fruit with polyphenols and essential oils extracted with Microwave Assisted Extraction technique

★★

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Abstract

Foods and beverages rich in polyphenols are potentially beneficial to human health [1].
Polyphenols and essential oils could take part in the food prevention of fresh-cut fruit with an additional nutrients value. Berries in general are one of the fruits with the highest phenolic content. Even though during the pressing treatment some phenolic compounds are moved into the juice, most of these remain in waste biomass. For this reason, berries pressed pulp are a great and valuable resource. To extract most of the polyphenolic content, a more efficient extraction is required.
To this aim, the study was focused on a green water-based microwave assisted extraction. Microwave hydro-diffusion was performed in a Milestone Ethos Up microwave laboratory oven consisting in a multimode microwave reactor operating with variable power (10 W increments, maximal value: 900 W). During the extraction, temperature was continuously monitored and recorded by an infrared sensor.
After the extraction, the biomass and the water enriched with polyphenols was split and Total Polyphenol Content was estimated by the Folin–Ciocalteu method. This enriched water was used for soaking wet fresh-cut fruit. This operation was done in order to evaluate the antioxidant power of the polyphenols on fresh cut fruit during time. Fresh-cut fruits (apple slices) was preserved into a closing packaging placed in a refrigerating environment. Organoleptic properties and total polyphenols content on the apple slices were monitoring during time.
In addition, tests with the addition of ascorbic acid were performed, in order to evaluate some differences from the polyphenol's tests.

The final goal is to create an innovative packaging enriched with polyphenols and essential oils aimed to fresh-cut fruit preservation. These compounds could have and antioxidant action on the fruit and could add nutritional and organoleptic properties to the final product.

Keywords

Waste management, polyphenols, essential oils, green extraction, circular economy

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Lipases And Cardoon: A Green Way To Obtain Bioplasticizers

* * *

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Abstract

The plastic request is continuously growing and with it the demand for plasticizers and lubricants. Only a small percentage of plastics, plasticizers and lubricants present on the market are bio-based or biodegradable, representing therefore a big issue for pollution and human health. It is well known that plant oil, through epoxidation of glycerides and free fatty acids, can be used as plasticizers or lubricants [1]. The oil extracted from *Cynara cardunculus* seeds, a typical plant of the Mediterranean area, is rich in linoleic and oleic acids, represent a promising biomass-derived feedstock to produce bioplasticizers and biolubricants.

In the field of transformation of renewable resources, such as plant oils, biocatalysis constitutes a powerful tool by taking advantage of the high selectivity and catalytic activity of enzymes [2]. In this project chemo-enzymatic epoxidation of cardoon oil is exploited to overcome the drawbacks of chemical processes, such as low selectivity, the formation of acidic byproducts, the low conversion yield, the use of unstable and explosive peroxiacids and the need of high temperatures [3]. In fact, in the enzymatic step, the formation of stable peracids takes place in situ by means of the reaction of H_2O_2 with free fatty acids, allowing for a significant suppression of side reactions. To obtain epoxidized triglycerides and fatty acids, two different strategies are applied: direct epoxidation of the oil in solvent-less condition, or prior enzymatic hydrolysis of fatty acids and their subsequent epoxidation. The point of force of both strategies is the use of immobilized lipases at mild temperature and solvent-less conditions, and the re-usability of the biocatalyst. Moreover, the protocols make use of lipases immobilized on rice husk, a renewable raw material derived from rice processing [4]. In this scenario, a fully "green process" will be applied to obtain high added value bioplasticizers and biolubricants starting from an inexpensive renewable biomass-derived material.

Figure: "Green process" to obtain bioplasticizers and biolubricants starting from cardoon oil.

Keywords
Enzymatic epoxidation, bioplasticizers, biolubricants, enzyme immobilization, cardoon oil

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Pb(II) adsorption of Eco-friendly composite beads

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Abstract

Present work, we propose the preparation of zeolite alginate beads and its adsorption performances of Pb(II) from aqueous solution. The alginate beads containing mesoporous zeolite was prepared by egg box method where extra-frame ionic gelation and zeolite powder encapsulation occurs at the same time [1,2]. Natural zeolite particles were enhanced by mechanic modification of the ball milling process without chemical additive [3]. Adsorption experiment was conducted in batch reactor with 100-500 ppm initial concentration of Pb(II). FTIR and SEM-EDS analyses confirmed that mechanically modified zeolite particles were incorporated into alginate hydrogel. The highest adsorption amount of zeolite alginate beads was 87.47 mg/g after 20 h adsorption process. SEM-EDS result confirmed that the adsorption process has occurred on the surface of zeolite alginate beads. Adsorption kinetic data were fitted with Langmuir adsorption isotherm which showed that Pb^{2+} cation adsorbed into monolayers of adsorbent material. Moreover, we observed that calcium ion released after the Pb^{2+} adsorption process in the feed solution. Therefore, the adsorption mechanism of zeolite alginate beads explained by complex mechanisms including surface sorption and ion exchange of Pb^{2+} and Ca^{2+} in beads. In conclude, zeolite alginate beads material can be an eco-friendly and cost-effective material for practical application.

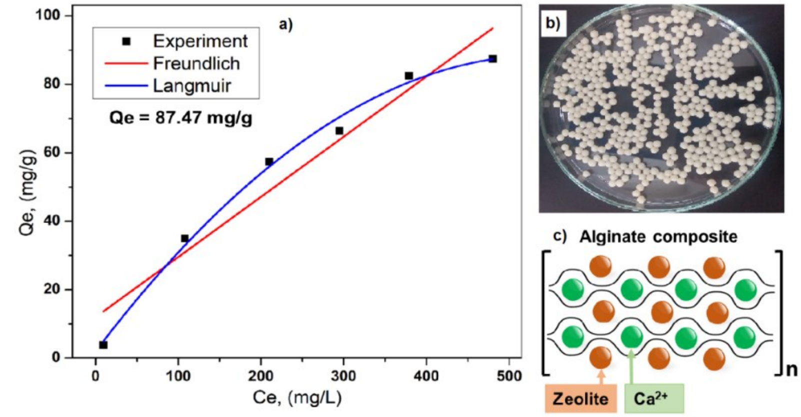

Figure 1. a) Adsorption isotherm of zeolite alginate beads (ZAB), b) ZAB, and c) ZAB structure.

Keywords: Natural zeolite, Pb(II) adsorption, alginate beads, mechanical modification

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Breaking the limit of lignin monomer production *via* cleavage of interunit carbon-carbon linkages

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Abstract

Conversion of lignin into monocyclic hydrocarbons as commodity chemicals and drop-in fuels is a highly desirable target for biorefineries. However, this is severely hindered by the presence of stable interunit carbon-carbon linkages in native lignin and those formed during lignin extraction. Herein, we report a new multifunctional catalyst Ru/$NbOPO_4$ that achieves the first example of catalytic cleavage of both interunit C-C and C-O bonds in one-pot lignin conversions, yielding 124-153% of monocyclic hydrocarbons; that is 1.2-1.5 times those yields obtained from the established nitrobenzene oxidation method. This catalyst also exhibits high stability and selectivity (up to 68%) to monocyclic arenes over repeated cycles. The mechanism of the activation and cleavage of 5-5 C-C bonds in biphenyl, as a lignin model adopting the most robust C-C linkages, has been revealed *via in situ* inelastic neutron scattering, coupled with modelling. This study breaks the conventional theoretical limit on lignin monomer production.

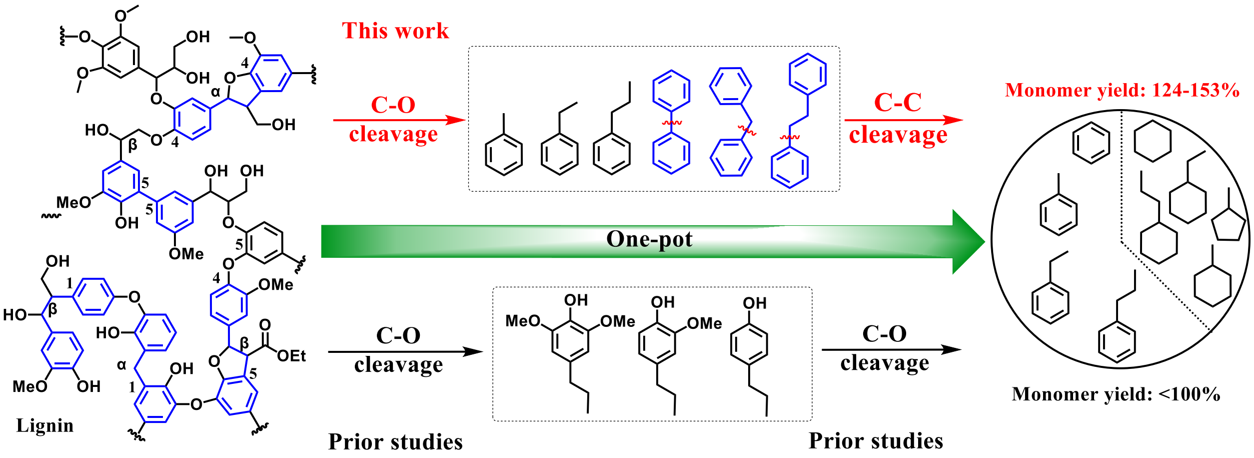

Figure 1. View of a representative structure of a lignin fragment, showing various intramolecular linkages and schematic representation of the one-pot depolymerisation and hydrodeoxygenation of lignin into monocyclic aromatic hydrocarbons.

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Cellulose dissolution by a new phosphonium-based deep eutectic solvent: a step towards industrial sugars production

★★

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Abstract

The presence of β-1, 4-glycosidic linkages in the structure of cellulose in the cell wall of lignocellulosic biomass encourages the formation of strong hydrogen bonds between cellulose chains, which makes it difficult for chemical or biological (enzymes or bacteria) attack, leading to depolymerization of the cellulose to sugars for subsequent processing into value-added products [1,2].

Several approaches and technologies have been considered for developing economical pretreatment methods for generating high yields of industrial sugars and value-added products such as HMF from cellulosic biomass, in order to reduce the use of fossil fuels [3]. The use of Ionic Liquid (IL) analogues known as Deep Eutectic Solvents (DES) in the dissolution of cellulosic biomass has gained increasing attention since their advent. This is due to their non-volatility, biodegradability, recyclability and non-reactivity [4]. ILs and DESs has been reported to show decrease in cellulose crystallinity by disrupting the hydrogen bonds in cellulose fibrils more than other pre-treatment methods [5].

DESs are generally solvent systems formed from the complexation of a salt (formed from any ammonium, sulfonium or phosphonium cation and a Lewis base usually a halide ion) with a hydrogen bond donor (HBD) such as amines, alcohols, or carboxylic acids [6, 7].

Herein, we present a new DES capable of dissolving cellulose which opens the opportunity to efficiently hydrolyze cellulose to industrial sugars.
The dissolution of cellulose in a phosphonium-based deep eutectic solvent has been demonstrated proving that DESs indeed have promising potential in the valorization of cellulosic biomass. An amount of 0.92 wt% of cellulose was dissolved in the DES. A decrease in its crystallinity is observed for both dissolved and undissolved cellulose indicating that it would be simple to subsequently hydrolyze the cellulose or chemically modify it to obtain value-added plant-based products.

Keywords: Deep eutectic solvents, lignocellulosic biomass, dissolution

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The use of Green solvent (Molten Hydrate Salt) in the one pot bioconversion of waste corn cob to succinic acid

★★★

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Abstract

Currently, production of succinic acid is a multi-stage process involving pretreatment, solid/liquid (S/L) separation, solids washing, liquid detoxification, neutralization, enzymatic hydrolysis and fermentation. These stages are responsible for elevating the capital and operating costs. To alleviate this problem via process intensification, a "one-pot" process, which combines pretreatment, hydrolysis and fermentation in one unit but by-passes the need for S/L separation, washing, detoxification and neutralization steps, has been proposed [1]. This process enhances the potential for optimal production of succinic acid from lignocellulosic biomass. Recently, inorganic salts-based molten hydrate salts (MHSs) have emerged as promising media for saccharification of polysaccharides because of the intrinsic acidity of the media [2]. This means that MHS solvents can effectively catalyze the hydrolysis of cellulose into glucose and hemicellulose into hexose in homogeneous and heterogeneous systems. This has opened new avenues for the study of "one-pot" bioconversion configuration wherein lignocellulosic feedstock is pretreated, hydrolysed and fermented simultaneously in one vessel. This research aims to investigate the use of MHS solvent systems in the production of succinic acid from corn cob by a single succinic acid producing bacteria (*Actinobacillus succinogenes)* as well as a mixed bacterial culture. The most effective MHS solvent was chosen based on cellulose retention as well as hemicellulose hydrolyzation with the aim of increasing the yield of succinic acid end product. The results showed that $ZnCl_2.4H_2O$/ Urea is the most efficient solvent tested recovered high % cellulose in solid and high % hemicellulose in liquid fraction and optimized conditions were at 120 °C, 90 minutes and solvent concentration of 74% $ZnCl_2.H_2O$/ 26% Urea. The results show MHS $ZnCl_2.4H_2O$/ Urea as a promising solvent for integrated "one-pot" bioconversion.

Keywords

Pre-treatment, Molten hydrate salt, Succinic acid

Acknowledgements

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Modification of starch via the Biginelli multicomponent reaction

★★★

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Abstract

Starch is one of the most important and abundant renewable polymers with outstanding features (e.g. renewability, biocompatibility, high thermal stability and low cost). Nevertheless, bottlenecks such as low solubility in organic solvents, high hydrophilicity and brittleness makes it not feasible to be processed. Therefore various chemical modifications like esterification, etherification, etc. have been developed to overcome the mentioned problems.[1] Quite recently, multicomponent reactions (MCRs) emerged as a powerful tool to prepare tailor-made, multi-functionalized (bio)polymer architectures offering high molecular diversity in a one-pot synthesis and elegant manner under considerably mild and sustainable conditions. Indeed, the Biginelli Multicomponent Reaction is one of the benchmarks MCRs,[2,3] which facilitates the synthesis of heterocyclic compounds, by using an aromatic aldehyde and a β-keto ester in the presence of urea and a catalyst.

In order to achieve a Biginelli type heterocyclic modification of starch, an acetoacetate derivative of starch is synthesized and further reacted with urea and various (partially) renewable and commercially available aldehyde derivatives to demonstrate the versatility of the method. In-depth analytical characterization via NMR, SEC and FTIR confirms the successful synthesis of Biginelli-starch derivatives. In summary, we demonstrate that it is feasible for starch polymers to be readily functionalized under metal-free and considerably mild conditions, thus yielding otherwise challenging-to-access starch architectures.[4]

Keywords Starch, Renewable Resources, Multicomponent Reactions

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Bio-Inspired Facile Green Fabrication Of Gold Nanoparticles Using The Leaf Extract Of Combretum Sp., Its Antibacterial Evaluation And Biocompatibility

★★★

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Abstract

A simple, green and cost-effective method for the synthesis of gold nanoparticles (AuNPs) using various volumes of the aqueous extract of *Combretum erythrophyllum* plant leaves as both the reducing and capping agents is herein reported for the first time. The as-prepared Ag-NPs were characterised using Ultraviolet–Visible (UV–Vis) absorption spectroscopy, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and dynamic light scattering (DLS) techniques. An immediate reduction of the gold salt was observed upon the addition of the plant extract with an absorption maximum of 530 nm. The TEM micrographs showed that the particles are mono dispersed and spherical in shape with an average particle diameter of 10.76 nm at 1 mL plant extract and 26.08 nm at 2 mL plant extract. The as-synthesised AuNPs showed efficient antibacterial activities against *Klebsiella pneumoniae*, a pathogenic microorganism which is implicated in infectious diseases. The cytotoxicity assay showed that the as-synthesized AuNPs showed biocompatibility towards normal cells (BHK-21) and cancerous cells (A549 and HeLa).

Keywords: Combretum erythrophyllum, Klebsiella pneumoniae, Gold nanoparticles

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Greener methods for lignin valorization: electrochemical upgrading of lignin monomers to valuable intermediates

Mahlet GAREDEW

Abstract

Conventional biomass to ethanol conversion strategies require the use of chemical pretreatments to improve sugar hydrolysis and enable lignin recovery. Though direct combustion of lignin is an option, deriving higher value fuels and chemicals is desired as lignin is one of the largest natural sources of renewable aromatic compounds. Achieving this requires the upgrading of lignin-derived phenolic intermediates via deoxygenation and hydrogenation or via oxidative cleavage to form valuable platform chemicals. Electrocatalysis offers a sustainable way to integrate renewable energy sources such as wind and solar with lignin depolymerization processes. Using electrocatalysis, abundant low-value lignin intermediates can be used to capture excess renewable electricity in the form of chemical bonds and converted to chemicals, fuels, and energy storage compounds. Furthermore, this process offers the opportunity to avoid harsh conditions that are often associated with catalytic processes, further reducing energy inputs. Because lignin is converted to phenolic monomers and dimers upon depolymerization, the electrochemical transformation of model compounds exhibiting similar bonding arrangements indicates the potential for both electrocatalytic hydrogenation (ECH) and electrocatalytic oxidation (ECO) of biomass lignin valorization. To this end, we report on the electrochemical transformation of various lignin-derived phenolic intermediates to valuable precursors. Having uncovered surprising C-C bond cleavages at mild conditions, the outcome of this work will provide a better understanding of electrochemical systems as greener lignin valorization paths in the context of an integrated biorefinery.

Key words: Lignin valorization, electrocatalysis, integrated biorefinery

Sustainable O-formylation of alcohols using CO_2 as C1 building block

* * *

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Abstract

Valorization of CO_2 is receiving a considerable attention in green chemistry as a C1 building block in organic synthesis because it is abundant, non-toxic and renewable [1]. Its capture and activation are the most challenging step due to its stability and inertness. Borohydride is an interesting reducing agent which is capable of capture and reduce three molecules of CO_2 per reductant molecule in mild conditions [2]. Although H_2 shows the most favorable atom economy, borohydride is easier to handle and thus, the process doesn't need high pressure conditions becoming a less risky methodology.

The reaction of CO_2 and borohydride results in triformoxyborohydride, a compound already described as formylating and methylating agent of amines [3], [4]. However, the O-formylation of alcohols from CO_2 hasn't been widely explored yet, as only a few examples were described [5]. As alcohols are widely present in biomass derivatives, the interest of this reaction is based on the synthesis of value-added products from both, biomass and CO_2, carbon renewable sources. The produced formates are considered valuable compounds in industry [6]. In addition, formate group can be used as a protective or an activating group for further reactions.

In this project, CO_2 was activated using $NaBH_4$ through an adaption of a methodology previously described in literature [3]. Triformoxyborohydride ($^{-}BH(OCHO)_3$) was obtained and lately used to formylate different alcohols, which included renewable alcohols. The hole process is described in figure 1. Good to excellent yields were obtained for the formate esters synthesis.

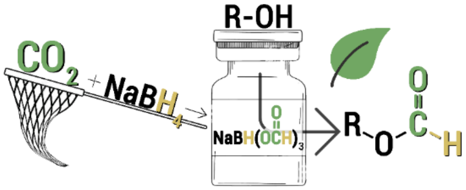

Figure 1

In conclusion, a sustainable and simple methodology for O-formylation of alcohols using CO_2 as C1 building block was developed. Formate esters are will be useful intermediaries to promote further reactions.

Keywords

O-formylation, CO2, alcohols

Acknowledgements

We thank Secretary of Science and Technology of Universidad Nacional de Córdoba (SeCyT-UNC) and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for financial support.

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Continuous flow tubular microreactor for the green synthesis of time-stable copper nanoparticles

★★★

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Abstract

Metallic nanoparticles are employed for many applications such as bio-sensing, electronics, catalysis, among others. Particularly, copper nanoparticles (CuNP) are of great interest as a non-expensive alternative to novel metal like Pt and Pd. CuNP have been applied in oxidation reactions, reduction of water pollutants, selective catalytic reduction of NO, as an antimicrobial nanomaterial, among others. However, CuNPs tends to agglomerate and oxidize easily under contact with air. Thus, changes in their physicochemical properties have a negative impact on its applications.

Controlling the synthesis conditions is a key factor to obtain small and time-stable nanoparticles. However, most of the reported protocols involve the use of toxic reducing and capping agents. Therefore, the transition to a green chemistry, employing new and optimized processes with less toxic reagents, is of major relevance. In this work, we employed starch as a sustainable, biodegradable, cheap, and non-toxic capping agent for the CuNP stabilization. Also, and in order to compare both set-up, the synthesis was carried out in a continuous microreactor (CuNP-M) and in a conventional round flask batch reactor (CuNP-B). The use of microfluidic devices allows to enhance the mass and energy transfer during the reaction, operating under safer conditions [1].

For the synthesis, copper acetate was employed as metallic precursor and an aqueous hydrazine solution was used as reducing agent. The use of N_2H_4 allows to carry out the reaction at room temperature, to fix only 1 minute as the residence time and forming N_2 as a non-toxic by-product.

The formation of CuNP was verified by UV-vis spectroscopy. The LSPR band between 585 and 620 nm, corresponding to nanometric metallic copper nanoparticles, could be observed for both set-up. The mean particle size was determined by Dinamic Light Scattering, indicating values of 10 nm and 13 nm for CuNP-B and CuNP-M, respectively. Following the stability by DLS, the mean particle size for CuNP-B changes from 10 nm to 150 nm after 14 days, indicative of an agglomeration process. However, the particle size of CuNP-M did not substantially change.

When using the microreactor, mass and heat transfer processes are more effective than in the conventional batch. The micro sized reaction volume tends to an optimal mixture of the reagents, with enhanced control of the nucleation, growth and stabilization of the nanoparticles.

On the one hand, XRD measurements indicate that in the batch round flask reactor, not only Cu was formed but also CuO and Cu_2O were detected. On the other hand, the microreactor device formed mainly metallic copper nanoparticles. Only a slight diffraction peak of CuO was detected. This could be related that in the microreactor, contact with the air is avoided and the highly reducing conditions preserve the CuNP against oxidation.

In conclusion, we demonstrated that CuNP can be obtained even at room temperature employing microreactors and environmentally friendly protocols. The use of microfluidic devices allows to enhance the reaction conditions, forming time-stable and non-oxidized nanoparticles, following the remarks of the green chemistry principles.

Keywords: Microreactors, copper nanoparticles, green synthesis.

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Copper-catalyzed reductive functionalization of CO_2 with amines: ligand effect on *N*-methylation and *N*-formylation

★★★

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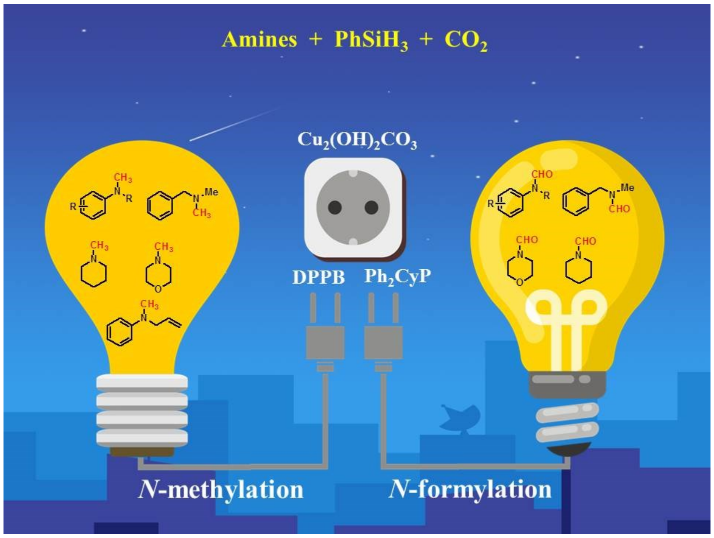
Abstract

Reductive functionalization of CO_2 is an attractive strategy to enlarge the product scope from CO_2. As different product may be obtained depending on the reduction level of CO_2, regulating the product selectivity has drawn considerable attention[1]. In this work, we have developed an alternative strategy for switching the reaction between *N*-methylation and *N*-formylation by choosing ligand in performing the Cu(I)-promoted reductive functionalization of CO_2[2]. With $Cu_2(OH)_2CO_3$ as catalyst precursor and phenylsilane as reductant, the ligand DPPB promotes *N*-methylation with high yield (up to 93%) and selectivities (up to 99%); while the ligand Ph_2CyP allows *N*-formylation with high yields (up to 98%) and selectivities (up to 99%). Both secondary aromatic amines and aliphatic amines can be methylated and formylated. Nitro- and allyl- group tolerance was performed in this system. Mechanistic study suggests that formamide would be the key intermediate for the *N*-methylation, and the selectivity depends on whether formamide could be further reduced. Accordingly, the ligand effect on regulation in the reductive functionalization of CO_2 provides an alternative clue for efficient metal-catalyzed selective CO_2 transformation.



Scheme 1. Ligand effect on *N*-methylation and *N*-formylation in reductive functionalization of CO_2 with amines

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Producing Ethylbenzene from Lignin

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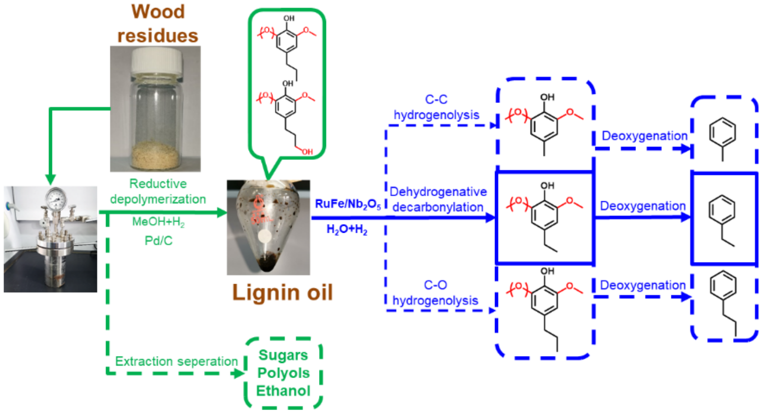
Abstract

The rising global concerns on energy and environment have intensified the interest in the utilization of clean and renewable energies. Lignin is the only renewable source of aromatic carbons in nature, and its conversion to a variety of value-added chemicals and liquid fuels has attracted increasing attention. Generally, the production of arenes from lignin or its-derived compounds undergoes hydrogenolysis and hydrodeoxygenation [1]. To avoid the ring-saturation, the direct deoxygenation pathway (DDO) is preferred during the reaction, which requires the weak adsorption of aromatic ring by the metal sites and the excellent oxophilic ability of the support [2].

We developed an efficient FeO_x modified Ru/Nb_2O_5 catalyst for selectively converting birch lignin oil (BLO) into ethylbenzene through two consecutive catalytic steps that involve dehydrogenative decarbonylation and hydrodeoxygenation (Figure 1) [3]. Compared with Ru/Nb_2O_5 catalyst, $RuFe/Nb_2O_5$ exhibited higher selectivity (or distribution) of ethylbenzene from both lignin model compound (78.5 %) and BLO (63.4 %). Various characterizations showed that the introduction of FeO_x species decreased the ratio of metallic Ru^0 species that restrained the direct hydrogenolysis of $C_{propanol}$-O bonds and enhanced the DHDC process. Moreover, the modification of FeO_x enhanced the oxygen vacancies on the surface of Nb_2O_5, thus promoting the cleavage of $C_{aromatic}$-O bonds. Both effects led to the highly selective production of ethylbenzene. Moreover, the rational design of $RuFe/Nb_2O_5$ catalyst provides a promising approach for the production of ethylbenzene from biomass resources.

Figure 1. Production of ethylbenzene from birch wood.



Keywords

Lignin oil, ethylbenzene, hydrodeoxygenation.

Acknowledgements

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Recycling Agricultural Wastes and By-products in Organic Farming

★★★

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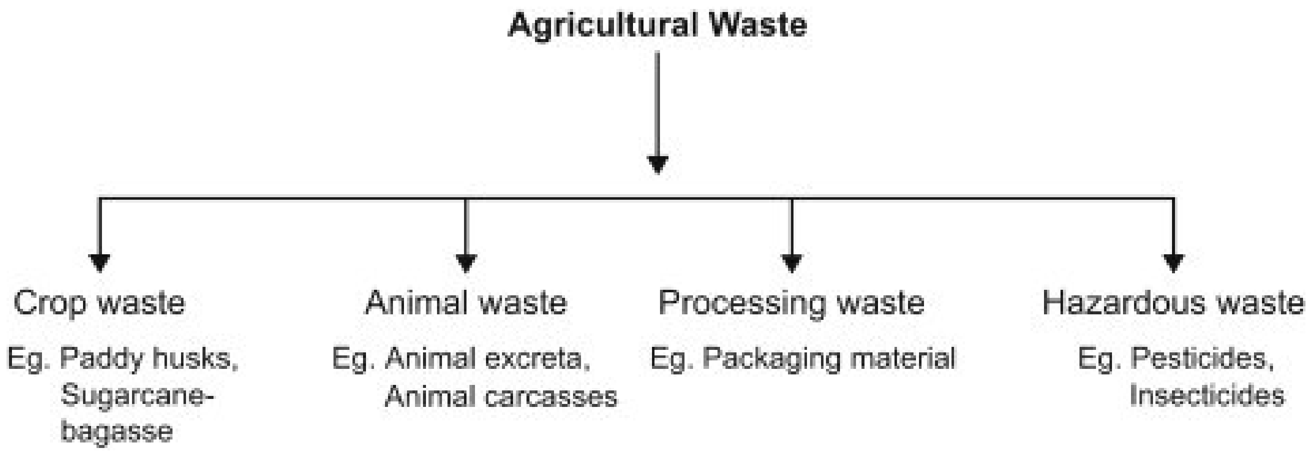
Abstract

The Circular Economy concept implies the re-design of existing production systems in agriculture, by promoting agricultural waste recycling. two different agroecological tools were considered: biofertilizer and presence or absence of green manure (GM+ and GM−). Moreover, the microorganism activity lasts for the whole composting process, where microorganism digest or decompose organic matters. therefore, as one of economical agricultural waste disposal method, composting is only suitable for organic agricultural solid waste.

And the organic agricultural waste can be: (i) Organic waste from farmland: Straw, wheat straw, corn straw, vegetable leaves; (ii) Animal farm organic waste: Chicken manure pig manure, cattle manure, horse manure, sheep manure; (iii) Organic waste from plantation: Leaves and small branches, rotten fruit. Therefore, the common agricultural waste disposal methods include burning, dumping, land filling, random piling. All these methods may cause pollution and waste of resources. Above mentioned wastes contain multiple nutrient elements, which can be made into organic fertilizer. meanwhile, the organic fertilizer can be used for agricultural production again. Therefore, it is an economical and environmentally friendly agricultural waste disposal method to deal with waste by composting.

Keywords: microorganism digest; biofertilizer; economical agricultural waste; Organic waste.



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Efficient solvent-free transfer hydrogenation of bio-derived furfural to furfuryl alcohol by Pd(II) and Pt(II) complexes

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Abstract

Pd-based and Pt-based catalysts are becoming increasingly popular as superior catalysts in hydrogenation of furfural.[1-4] The majority of the reported catalyst systems are heterogeneous in nature which exhibit low selectivity for the desired products and require high pressure and temperature operating conditions for practical use.[5] To the best of our knowledge no literature has been reported on the use of homogeneous Pt-based catalysts for hydrogenation of furfural. In this work, Pd(II) and Pt(II) complexes have been synthesized and characterized using nuclear magnetic resonance spectroscopy ^{1}H NMR, ^{13}C{^{1}H} NMR and ^{31}P{^{1}H} NMR, infrared spectroscopy, high resolution electrospray ionisation mass spectrometry as well as elemental analysis. These complexes were evaluated as catalyst pre-cursors using formic acid as a hydrogen source. Both catalytic systems **C1** and **C2** resulted in good activity and exclusive selectivity towards furfuryl alcohol in the hydrogenation reaction. The highest turnover frequency obtained was 1060 h^{-1} using pre-catalyst **C2**. *In situ* NMR studies were performed and culminated in the proposition of a plausible reaction mechanism for the transformation.

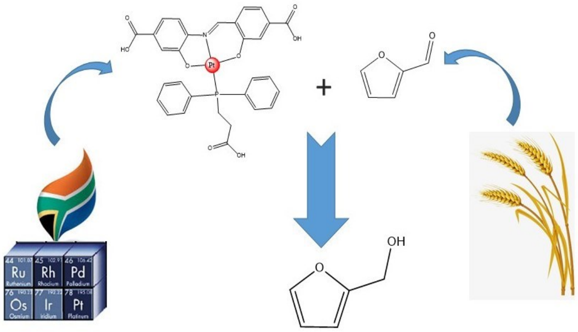

Figure 1. Transfer hydrogenation of furfural to furfuryl alcohol

Keywords: Homogenous, palladium, platinum, furfural hydrogenation, furfuryl alcohol.

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Vanillin acrylate-based photocross-linked polymers

★★★

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Abstract

Vanillin is currently one of the only biobased and aromatic compounds that are industrially available [1]. In this study vanillin derivatives, vanillin diacrylate and vanillin dimethacrylate, were used for thiol-ene and free radical photopolymerizations to obtain new biobased polymers. The kinetics of photocross-linking was investigated by real-time photorheometry using three photoinitiators ethyl(2,4,6-trimethylbenzoyl)phenylphosphinate, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide or phenylbis (2,4,6-trimethylbenzoyl)phosphine oxide in different quantities.

The chemical structure of obtained polymers was confirmed by FT-IR spectroscopy. The yield of insoluble fraction obtained after Soxhlet extraction with acetone after 24 hours was in the range of (77-96) %. The cross-linking density, calculated from real-time photorheometry storage modulus curve at the steady state, was in the range of (49-7928) mol/m^3. Thermal and mechanical properties of vanillin diacrylate-based and vanillin dimethacrylate-based polymer films were investigated.

It was determined that vanillin diacrylate-based and vanillin dimethacrylate-based photocross-linked homopolymer films are more rigid and mechanically stronger, whereas vanillin diacrylate-based and vanillin dimethacrylate-based photocross-linked copolymer films with 1,3-benzenedithiol are more soft and flexible. Thermal and mechanical properties of vanillin-acrylate based polymers were comparable with those of commercial petroleum-derived materials used in optical 3D printing.

Keywords: vanillin acrylates, photopolymerization, optical 3D printing

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Valorisation of Biomass to Furfuryl Alcohol

★★

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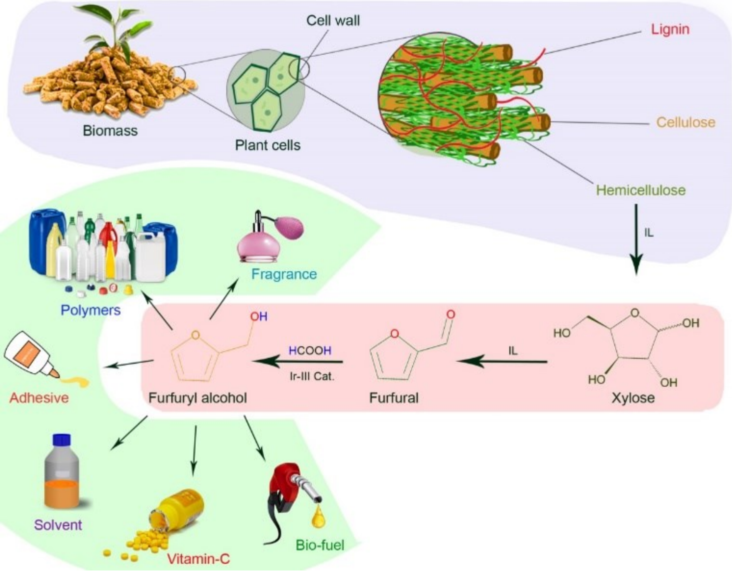
Abstract

The sources of carbon for the production of fuels and chemicals have for the past century been derived from fossil resources (coal, crude oil and natural gas).[1] However, burning of these fossil products causes environmental pollution and also has a great impact on the climate. To avoid these problems, scientists are looking towards the utilization of alternative sources of carbon for the production of fuels and chemicals.[2] Plant biomass is an important alternative source of carbon that contains carbohydrate polymers and can be to transformed into many chemicals including ethanol, sorbitol, 2,5-hydroxymethylfurfural, levulinic acid and furfural.[3,4] In turn, furfural can be converted into furfuryl alcohol which has many applications in various industries. It is used as a solvent and also serves as an intermediate in the production of thermostatic resins, adhesives, plasticizers, fragrances, vitamin-C and bio-fuels.[5] The transformation of carbohydrate polymers and their monomeric sugars usually requires acid catalysed hydrolysis and dehydration with the aid of mineral acids. The use of mineral acids, however, causes reactor corrosion and formation of insoluble humins.[6] Hence the need for other sources of acids is vital. Ionic liquids have gained popularity in this regard since they have the added advantage of dissolving raw biomass, and would therefore perform multiple dissolution-hydrolysis-dehydration functions when possessing acid functionalities. Herein, we report on the exploration of ionic liquids (IL) in the transformation of raw biomass to furfural. This will then be further upgraded *via* hydrogenation with pyridinyl-imine iridium(III) complexes.



Scheme 1: From plants to chemicals

Keywords: *Biomass, Ionic liquids, hydrogenation, Recyclable catalysts,*

Acknowledgements: This work was supported by the Royal Society and African Academy of Sciences, the Future Leaders—African Independent Researchers (FLAIR) Scheme (Fellowship ref.: 191779), the National Research Foundation (NRF) of South Africa (Grant numbers: 112809 and 117989) and the University of Johannesburg's Research Centre for Synthesis and Catalysis.

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Candlenut Shell Lignocellulosic Valorization

★★

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Abstract

Biomass has surfaced as an important renewable feedstock for fuels and chemicals, especially due to the depletion of fossil fuels and concern with climate change mitigation [1]. Lignocellulose is particularly attractive since its use competes minimally with food production [2]. An integrated bio-refinery can be imagined, within which cellulose, hemicellulose and lignin would be efficiently utilized towards energy, fuels, and chemicals/materials production [1]. A lot of efforts have been reported towards this goal, which highlighted important challenges of lignin valorization, often related to the lignin structural complexity and heterogeneity [1-2]. These difficulties are enhanced during pulping processes that separate lignocellulose into its primary components [1].

Our research aims to bypass the challenges associated with lignin complexity resultant from pulping processes by developing a tandem delignification/depolymerization reaction on raw unfractionated lignocellulose. Our goal is to generate a processable carbohydrate pulp along with valuable lignin-derived aromatics (monomers and oligomers). We aim for a sustainable process by using an abundant and inexpensive heterogeneous copper-based catalyst, as well as reagents and solvents that can be derived from renewable sources. We present this work making use of candlenut shells, waste biomass generated from biodiesel production, which were recently discovered to contain a catechol-based lignin, termed C-lignin, in addition to guaiacyl and syringyl-type lignin [3]. Hence, we demonstrate the development of our methodology while optimizing to reach selectivity between catechyl versus guaiacyl target products.

Keywords

Lignin, Reductive Catalytic Valorization, Catechols

Acknowledgements

We would like to acknowledge the Yale School of Environment for financial support, as well as the African Power Initiative for donation of the biomass.

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ADMET polymers from sugars and castor oil [1]

* * *

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Abstract

Natural monosaccharides with unmodified backbone were used for the synthesis of renewable polymers. D-xylose and D-mannose (obtainable from second generation feedstocks) were used for the synthesis of α,ω-unsaturated glycolipids combining a rigid isopropylidene-functionalised carbohydrate core with flexible 10-undecenoic acid chains (from castor oil). These monomers were polymerised via acyclic diene metathesis (ADMET) with Grubbs second generation catalyst. Using low catalyst loadings (0.1 mol%) and no solvents (with associated sustainability and cost benefits), high molecular weight (Mn up to 71 kg mol^{-1}) amorphous polyesters were obtained, with high thermal (up to 365 °C) and hydrolytic (pH 7, 0, 14) stability, and relatively low glass transition temperatures (–28 to –8 °C), imparted by the flexible fatty acid chain. Post-polymerisation modification via ketal deprotection revealed hydroxyl groups inducing semicrystallinity, allowing the production of transparent polymer films. Further hydroxyl functionalisation (including with phosphine groups) was demonstrated, opening new possibilities for functional renewable polymers.

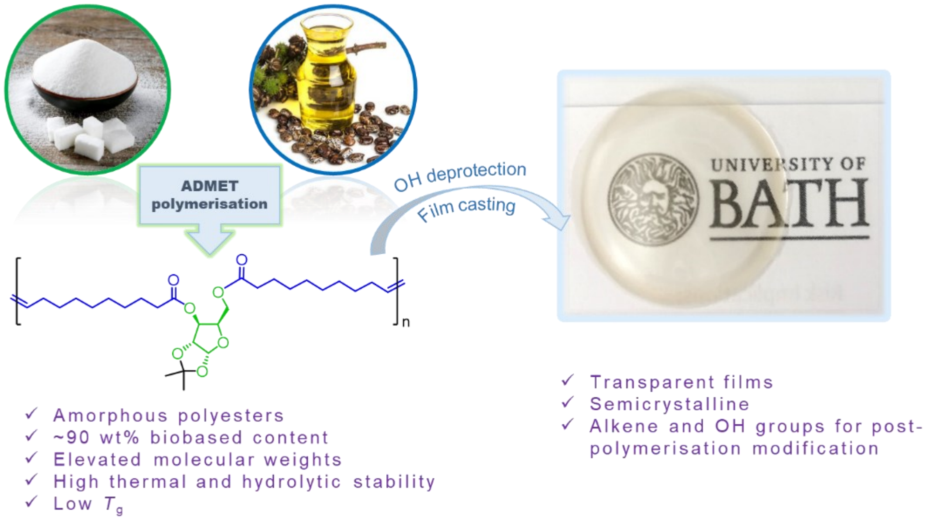

Figure 1. Graphical abstract

Keywords: Sugar-based polymers, second generation feedstocks, ADMET polymerisation

Acknowledgements

This work was supported by the UK Engineering and Physical Sciences Research Council (EPSRC) EP/L016354/1 (Studentship to MP, CDT in Sustainable Chemical Technologies). Analytical facilities were provided through the Material and Chemical Characterisation Facility (MC^2) at the University of Bath.

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Valorisation of CO_2 in the cycloaddition to epoxides using MgO nanocatalysts

★★

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Abstract

During the past century, the intensification of human activities along with the use of fossil fuels as primary source of energy caused the CO_2 concentration in the atmosphere to drastically increase. Capture, sequestration, and valorisation of this greenhouse gas are of primary importance to achieve the zero net global emissions urged by the Intergovernmental Panel on Climate Change in their last reports. The use of CO_2 as a source of carbon for chemistry is tricky: it is a very stable molecule. To overcome this, the use of catalysts is often required. We investigated step by step a promising pathway toward the valorisation of CO_2, starting from the synthesis of an available eco-friendly heterogeneous catalyst, to its use in the cycloaddition of CO_2 to epoxides to form cyclic carbonates.

Magnesium oxide nanoparticles are promising catalysts thanks to the natural affinity of alkaline earth-oxides with CO_2 (due to the presence of both acid and basic site on their surfaces), to the availability of magnesium (one of the most abundant element on earth) and to the low hazard nature of magnesium oxide. By adapting a procedure reported elsewhere[1], we obtained nano-sized MgO, with an average crystallite size of 12 nm, by precipitation of $Mg(NO_3)_2$ salt in basic aqueous conditions followed by calcination at 500 °C. The catalyst was used in the cycloaddition of CO_2 to 2,3-epoxypropylbenzene to form the corresponding cyclic carbonate (4-benzyl-1,3dioxolan-2-one) under 5 bars of CO_2, at 150°C and without solvent. This reaction limits the produced waste: the heterogeneous catalyst can be easily isolated and recycled by thermal treatment, cycloadditions produce a pure product and no solvent is required. The low catalyst activity is currently the main issue: it takes several days to reach a conversion of 70 % with 0.15 equivalent of catalyst in these conditions. Fine tuning of the catalyst properties (size, morphology, crystallographic faces exposed, surface state, etc.) is now necessary to maximize its activity. We have here the first blocks of a valorisation pathway for CO2 respecting the general principles of green chemistry. Optimisation is now necessary to show that this kind of reaction can be economically viable.

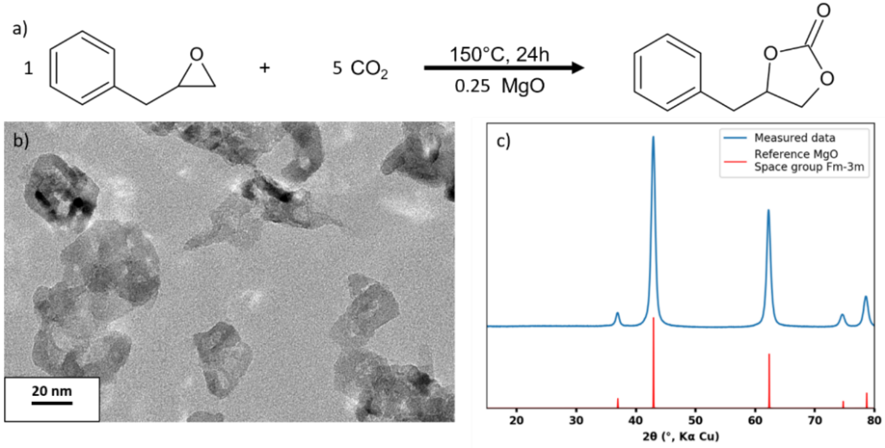

Figure 1: a) Cycloaddition of CO2 on 2,3-epoxypropylbenzene catalysed by nanosized MgO, b) TEM image of the MgO catalyst, c) XRD pattern of the MgO catalyst

Keywords: CO_2 valorisation, heterogeneous catalysis, waste reduction

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Valorisation of waste biomass for sustainable development

★★★

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Abstract

Climatic disturbances due to rapid use of non-renewable resources to meet the energy requirements has shifted the vision of scientists to explore the unexplored potential of renewable carbon-based resources i.e. biomass [1]. Globally, last few decades focus on profitable utilization of waste biomass to biofuels while contributing to bioenergy domain. A systematic approach considering the sustainability goals need to be studied to convert the waste biomass to chemicals and functional materials [1,2]. Development of an efficient recyclable catalytic system while valorising all lignocellulose constituents with low energy inputs is the current protocol for biomass conversion. This work is a critical analysis of different pretreatment methods and conversion technologies implemented to achieve value added chemicals such as bio-surfactants, green solvents, catalysts, fine and speciality chemicals, functional polymers, bulk chemicals etc. from waste biomass [3-5]. Different green chemistry tools such as process mass intensity, E-factor, V-factor etc. are overviewed with respect to feedstock and biomass valorisation technology which will result in the establishment of a sustainable and circular economy [1,2,5].

Keywords: Biomass; Valorisation; Green Chemistry; Sustainability; Circular Economy

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Preparation of new bio-based acrylate monomers to produce sustainable polymers.

★★

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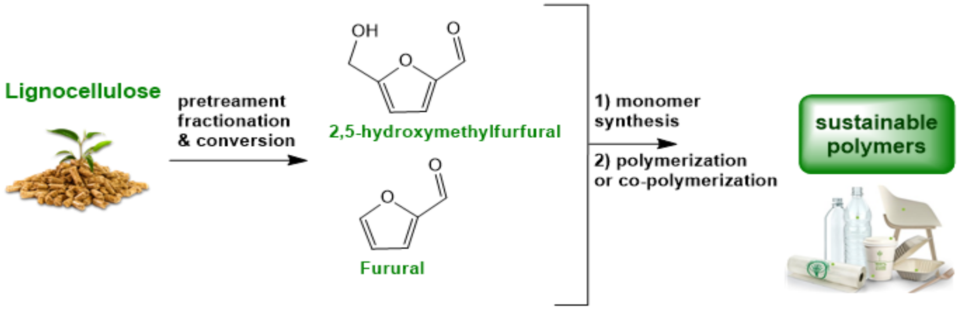
Abstract

The synthesis of monomers and polymers from renewable resources is nowadays a topic of intense research. This is due to the gradual depletion of petroleum resources together with environmental issues around global warming and environmental pollution.[1] As a result, traditional fossil fuel-based polymers with slow degradation reactions are being averted for biogenic or sustainable polymers that degrade readily in the environment.[2,3] Monomers such as carbon dioxide, terpenes, vegetable oils and carbohydrates can be used as feedstocks for the manufacture of a variety of sustainable materials and products, including elastomers, plastics, hydrogels, flexible electronics, resins, engineering polymers and composites.[4] Efficient catalysis is required to produce monomers, to facilitate selective polymerizations and to enable recycling or upcycling of waste materials.[5,6] Herein, we report synthesis of new furfural and glycerol based monomers and their subsequent polymerization and copolymerization to produce sustainable polymers.

Scheme 1: Synthesis of sustainable monomers and polymers from biomass.



Keywords: *Bio-based, Furfural, Glycerol, Polyacrylate, Renewable.*

Acknowledgements

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Recycling and re-use of waste materials in households and agriculture

★★

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Abstract

Wastes is anything that is considered as no more useful and needs to be disposed of. The term may include objects and materials that are no more fit for the primary use for which they were produced, as well as materials that are by-products. The proposed poster considers these two components of wastes with reference to households and agriculture in rural areas and presents various recycling examples.

Many rural areas in low-income countries have no or limited waste management or waste disposal services, and waste materials are mostly burnt in the open-air or dumped in the bushes. Burning wastes cause harm to the environment because of the emission of harmful gases and particulates. The dumping of household wastes into the surrounding areas also causes harm, because some of the materials present in the wastes do not decay, and because of the general littering outcome.

Recycling means finding new uses for materials or objects that are no more suitable for their primary purposes. At household level, containers of different types (plastic containers for foods, drinks or household chemicals, or boxes) can be used as containers for other purposes, or transformed into decoration objects. It is important to stimulate initiatives for this household recycling, and also to educate people to separate items that can be collected by recycling companies (such as aluminium cans, glass containers or paper) and store them until they get collected. There is also urgent need that plastics are included into these collections by recycling companies, because they are not degradable and are highly polluting if dispersed into the environment.

Wastes from agriculture are all biodegradable. On the other hand, they need to be removed when fields are prepared for the new sowing season. The current practice is that of burning them, which generates air pollution. Shifting to the practice of utilizing them for the purposes for which they may be suitable (composting turning them into fertilizers, small-scale biodigestors for the production of energy, animal feed, and others) would contribute to prevent environmental pollution and, at the same time, would bring an economic gain.

Keywords: recycling, rural contexts, waste materials, waste prevention

Production of Benzene Polycarboxylic Acids from Organosolv Lignin by Alkali-Oxygen Oxidation

★★

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Abstract

Nature efficiently synthesizes aromatic structures and deposits them as lignin in plant. As an amorphous macromolecule and the most abundant natural aromatic polymer compound, lignin is still largely regarded simply as a source for heat and power because of its chemical recalcitrance and structural complexity. It is very important to make good use of this organic substance.

Nowadays, lignin has been converted to phenols and arenes through catalytic reduction, also to vanillin and small molecular fatty acids through oxidation. When lignin was oxidized in our work, 11 benzene carboxylic acids (BCAs) was analyzed qualitatively and quantitatively by HPLC-ESI-MS. We investigated temperature, pressure, reaction time and alkali/lignin mass ratio to obtained the best yield of lignin with 7.94%. Although the yield of BCAs is relatively lower compared with other oxidation products, BCAs are firstly discovered during lignin oxidation. Besides, BCAs are important chemicals made from petrochemical industry, so the production of BCAs during lignin oxidation is very important for sustainable development.

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2. NEW REACTION PATHWAYS

A Scalable Phase Transfer Catalyzed Synthesis of a BAY 43-9006 Precursor: from Batch Microwave to a Flow Packed Bed Reactor

★★★

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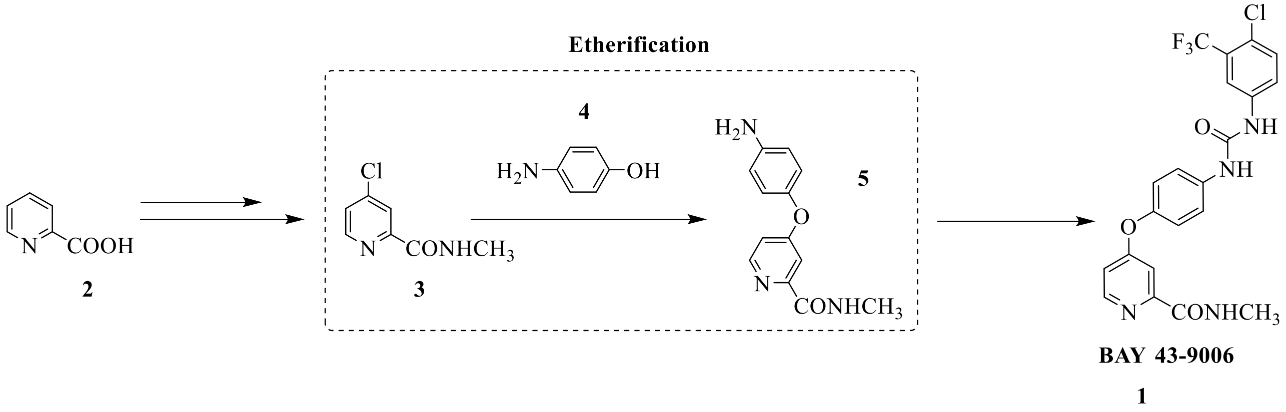
Abstract

Over the past 30 years, the batch-based synthesis of chemical compounds has been intensively pursued, with many synthetic methodologies and routes being developed. However, the synthetic technologies with the capability of scale-up for industrial application in the preparation of important chemical compounds are often not well established. Aspects such as industrial application feasibility, their cost and or environmental impact are often neglected, although they are key issues for industrial scale-up. Continuous flow processing is one kind of synthesis technique that has been reported to enable direct scale-up of reaction processes from lab to plant scale with multi-kilogram quantities of products generated in high throughput [1]. As such, this study is aimed at developing a scalable continuous flow process for the synthesis of a BAY 43-9006 precursor **5** (Scheme 1), a Raf kinase inhibitor used in the treatment of renal cell carcinoma, hepatocellular carcinoma and thyroid cancer [2-4]. Herein, we detail our strategy towards achieving the aforementioned.



Scheme 1 Synthetic approach towards BAY 43-9006 precursor **5**

Keywords

phase transfer catalyst, microwave synthesis, continuous flow, scale-up

Acknowledgements

We would like to thank Anton Paar for the benchtop-batch microwave equipment and the National Research Foundation South Africa for financial support.

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Energy efficient solid-state metathesis reactions for nanocarbide synthesis

★★★

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Abstract

Transition metal carbides have attracted great interest due to their mechanical and catalytic properties but their syntheses generally require energy-consuming processes with temperatures exceeding 800 °C, either for calcination or for carbon insertion [1,2]. We report here a recently developed solid-state metathesis reaction between a metal chloride ($ZrCl_4$, $NbCl_5$, $MoCl_5$, $HfCl_4$, $TaCl_5$, WCl_6) and potassium dispersed in carbon (graphite or acetylene black) [3]. The expeditious reaction is initiated at room temperature or with gentle heat activation. Under inert atmosphere, the potassium reduces the metal cation to form KCl salt and metallic or carbide nanoparticles (< 50 nm diameter) dispersed on a hydrophobic carbon support. In few cases ($ZrCl_4$, $NbCl_5$, $HfCl_4$, $TaCl_5$), the metal is further converted into a hydride upon neutralization of the reaction crude [4].

Beyond the advantages of this process in terms of green chemistry (no solvent, no heating, high atom efficiency and innocuous wastes), the reaction is versatile, gives access to ligand-free surfaces and can be applied to numerous early transition metals.

However, the process suffered from a lack of robustness and a poor understanding of the mechanism. In the present work, we studied the impact of different parameters (grain size of precursors, atmosphere, stoichiometry, dispersion of potassium…) on the metal speciation and the morphology of the nanoparticles. The objects are studied by Powder X-ray diffraction (PXRD) and by Transmission Electron Microscopy (TEM) (*cf.* Figure 1). We also aim at studying the catalytic properties of the obtained nanoparticles in reactions such as butadiene hydrogenation.

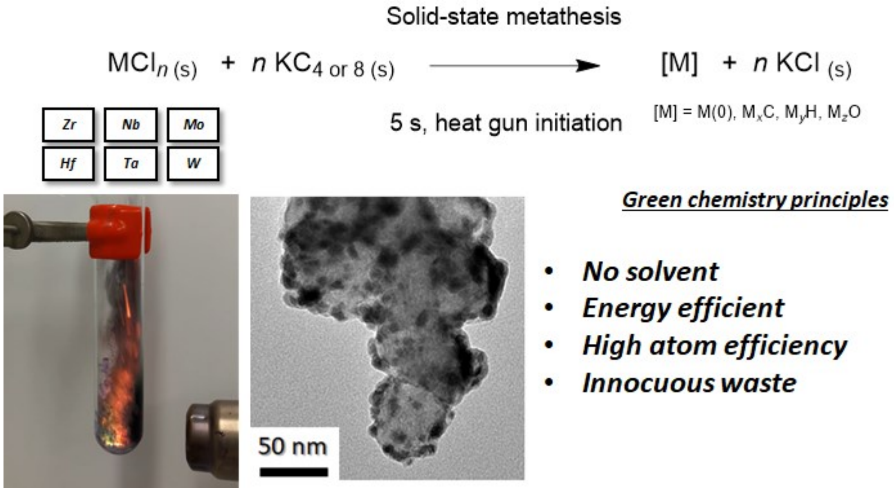

Figure 2: Solid-state synthesis of tungsten carbide nanoparticles on carbon support (left: movie snapshot of the reaction, right : transmission electron micrograph of a tungsten carbide sample)

Keywords: solid-state metathesis, energy efficient synthesis, carbide, hydride, nanoparticles

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Mustard Carbonates: One-pot reactions to pharmaceutical intermediates

* * *

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Abstract

Mustard Gases, bis-(2-chloroethyl)sulphide and bis-(2-chloroethyl)ethylamine, are unfortunately known for their use like chemical weapons during the Great War.[1]

Mustard Gases toxicity is strictly linked to their high reactivity. In fact, Mustard Gases can remove chloride ion through an intramolecular nucleophilic substitution thanks to the Neighbouring Group Participation (NGP or Anchimeric Assistance) of sulphur or nitrogen atom, forming an highly reactive three-member episulfonic or aziridine cyclic ion.[2] Although their extreme toxicity, Mustard Gases find application in pharmaceutical field like interesting reaction intermediates for synthesis of drugs.[3]

Using the chemistry of dialkyl carbonates (DACs)[4] - known as Green reagents and solvent - with Mustard Gases precursors (alcohols/diols), it permitted to synthetize a new class of compounds: Mustard Carbonates.

Mustard Carbonates conserve NGP but do not show any toxicity and danger for the operator, like demonstrated in several studies. The Mustard Carbonates - synthetized starting from precursor alcohol and DACs, in presence of base - were made react with different nucleophiles (-OH, -NH$_2$ and acid -CH$_2$).[5] The reactions were conducted in autoclave and in neat. Applications including synthesis of heterocycles through ring expansion reactions and macrocycles synthesis.[5]

Recently, reactions were investigated where Mustard Carbonates are synthetized in *situ* and alkylation reaction is tested in one-pot.

Due high pharmacological interest of Mustard Gases, we tried some several reactions for synthesis of possible pharmaceutical intermediates applying one-pot and/or double steps methodology, unifying DACs chemistry with anchimeric assistance.

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The (oligo)alkylation of oil fractions rich in aromatic hydrocarbons with C_6-C_{10} – olefins in the presence of ionic liquids

★★★

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Abstract

This thesis dedicated to the development of (oligo)alkylation processes of oil fractions rich in aromatic hydrocarbons (liquid fraction obtained reforming process) with α-olefins (hexene-1, octene-1, decene-1) in the presence of ionic liquids (IL) and the research of property of obtained products. As catalytic systems were used chloroaluminate (triethylaluminium chloride and pyridinium chloride) IL and nanometal - polymer composite (polyolefins containing Cu and Zn) was used in the catalytic system as a modifier and zinc chloride was used in the catalytic system as a component and were compared the obtained results. It has been shown that ionic liquid catalytic systems (ILCS) are acceptable for (oligo) alkylation reactions. They can be reused and depending on the composition, the molecular, thermophysical, and other characteristics of the obtained products can be regulated. The use of nanometal - polymer composite taken as a modifier improves the dispersibility of ILCS according to our investigations. This shows a great impact on two-phased catalytic systems. The selectivity of the target product increases. Obtained (oligo) alkylate products (OAP) identified by IR-, NMR-spectroscopy, DSC, GPC and different physical-chemical methods and are characterized by having an alkyl aromatics structure. Furthermore, the obtained OAP has been tested as a plasticizer additive in the composition of polyolefin composites. The thermophysical properties of various polyolefins and compositions based on OAP were determined. In each case, a drop in the melting point of the initial polyolefin matrix down to 20-30°C has been determined. It should be noted that in this circumstance the rheological properties of the polymer composite can be improved and easily processed. The composition of composites was determined by IRS, SEM, DSC, TQ, RFA and other methods. It has been shown that different polyolefin-OAP composites can be used as different polymeric materials, including phase transition materials in the future. So, it is identified that, (oligo)alkylation process can be carried out in the presence of ILCS by using directly oil fractions.

Keywords

Ionic liquids, liquid fractions obtained reforming, (nano)metal-polymer composites, (oligo)alkylation.

Acknowledgements

This work was performed within the "Polymerization catalysts" laboratory of the Institute of Petrochemical Processes named after acad. Y.H.Mammedaliyev of Azerbaijan National Academy of Sciences.

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Diffusion In Ionic Liquids - Aromatic Hydrocarbons Solutions By Molecular Dynamics Simulation

★★

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Abstract

Difficulties in the separation of aromatic and aliphatic carbohydrates from oil at temperatures above the boiling point are complicated by the processes of azeotropic compounds formation. Therefore, extraction or extractive distillation with polar organic solvents, such as NFM (Uhde Morphylane process), Sulfolane (UOP / Shell Sulfolane Process), NMP, ethylene glycols, etc. is used in the processing and separation of hydrocarbons. Another class of solvents that are considered promising for the replacement of organic solvents in industrial processes are ionic liquids (ILs). Modeling of aromatic hydrocarbons extraction processes from oil has shown that the use of the latest technological processes based on ionic liquids is more cost-effective [1]. Therefore, the aim of this work is a detailed study of structural and dynamic processes and energy properties of systems ionic liquid (1,3-dimethylimidazolium chloride dmim$^+$/Cl$^-$) - solute molecule (benzene, toluene, anisole) at T = 400K, at which the studied system is in liquid state.

The MD method was applied using a modified DL_POLY_4.05 with a time step of 2 fs. The long-range electrostatic interaction was taken into account by the Ewald method. In the calculations, the cations, anions, and atoms forming the molecules of the added substance (benzene, toluene, anisole) ware treated as solid charged model systems with a fixed geometry. The methyl in the dmim$^+$ and toluene ware treated as a pseudoatom with the total charge. All the studies were conducted for systems composed of 192 dmim$^+$ cations, 192 chlorine anions Cl $^-$, and one solute molecule at T = 400 K. The study of infinitely dilute solutions allows to clearly determine the mechanisms of interaction between the molecule of solute (benzene, toluene, anisole) and components of the ionic liquid, which allows to analyze the extraction of aromatic hydrocarbons and the influence of physical and structural properties at the micro level [2].

Analysis of the data allowed to establish:

(1) the nature of the motion of the solute and the mechanisms of diffusion in the studied systems are determined by the physical properties (mass and dipole moment) of the solute molecule.

(2) mobility of aromatic hydrocarbons dissolved in the ionic liquid correlates with the mass and value of the dipole moment of the aromatic hydrocarbon dissolved in the ionic liquid.

(3) based on the data obtained from RDF, MSD, VAF and FAF different diffusion mechanisms of solute molecules in IL were determined. At times less than 25 ps, the motion of aromatic hydrocarbon molecules (benzene, toluene and anisole) in dmim$^+$/Cl$^-$ can be represented within the same model representations, namely, as a result of inelastic collisions with IL components. At times t> 150 ps there is there is a change in the nature of the IL components motion and a change in the nature of the diffusion processes in this system depending on the physical properties of the dissolved substance. (4) dynamic inhomogeneity in the motion of a solute molecule in the dmim$^+$/Cl$^-$ system is associated with the transition from oscillatory processes in the motion of the molecule to translational, i.e. with a qualitative change in system dynamics and a change in the diffusion mechanism of solute molecules.

The results showed that IL had good ability in the extraction. Molecular structure of aromatic compounds was found to have a great influence on the extraction. Due to the increase of the hydrophobicity of solute, the partition coefficient of aromatic compounds was increased.

Keywords: diffusion mechanism, ionic liquids, aromatic hydrocarbons

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Reversible phase behavior modulation of azobenzene ionic liquid-based emulsions by UV/vis irradiation

★★★

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Abstract

The balance between the long-term stability of the emulsions and its reversible emulsification-demulsification is an important issue in the field of emulsions. Environmental stimulus responsive ionic liquid-based emulsions provide a new way to solve this problem.[1] The use of light as an external stimulus is of particular interest because light has noninvasive character and can be delivered remotely and precisely in space and time.[2] In this work, the photo-responsive emulsions were constructed by azobenzene-based ionic liquids, n-octane and water. It was found that, for a given ionic liquid, a stable emulsion could be formed when the concentration of the ionic liquid was above its critical micelle concentration, and the stability of the emulsion increased with increasing ionic liquid concentration. At a given concentration of ionic liquid, the stability of the emulsion is related to the number of ionic liquid methylenes.（Figure 1）.Upon UV irradiation, the emulsions underwent obvious demulsification, after further irradiation by vis-light, the system was emulsified again to form a stable emulsion. The structure of ionic liquids had a significant effect on the demulsification rate(Table 1).

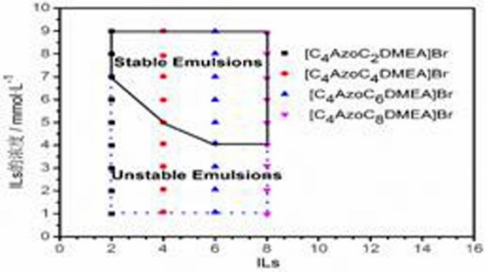

Figure.1. Phase diagram of n-octane/[C_4AzoC_nDMEA]Br/water emulsion system.

Table 1. Phase behavior modulation of emulsions by light.

ILs	Completely demulsification time
[C_4AzoC_2DMEA]Br	10min
[C_4AzoC_4DMEA]Br	2 h
[C_4AzoC_6DMEA]Br	8.5 h
[C_4AzoC_8DMEA]Br	12h incomplete demulsification
[C_4AzoC_2Py]Br	25min
[C_4AzoC_2TMA]Br	35 min
[C_4AzoC_2MIM]Br	40 min

Keywords

Ionic liquid; Emulsion; Photo-responsive; Phase behavior modulation

Acknowledgements

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Mechanochemistry: Versatile and Functional Strategy for the Realization and the Recycling of Multi-Phase Materials

★★

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Abstract

In the frame of the Circular Economy and Zero Waste concepts, waste materials and industrial byproducts are increasingly seen as valuable sources of secondary raw materials, to be reintroduced in the production cycle. Lignocellulosic biomasses from agro-industrial wastes have garnered increasing research interest because of their large availability and renewable nature: high value chemicals and additives can be obtained from their treatment. At the same time, the recycling of plastics from industrial and/or household waste represent an effective way to prevent their potential dispersion in the environment, recovering a part of their value through the transformation into new products. This is especially true for packaging waste, having a very short useful life and thus possessing excellent chemo/physical characteristics when disposed of.

Recent recovery and recycling strategies focus their attention on a green chemistry approach, pursuing the development of sustainable processes that reduce to a minimum the use of harmful chemicals, raw materials and energy.

With this in mind, mechanochemistry will be explored as an eco-friendly and economically viable methodology for the destructuration and recovery of lignocellulosic materials as well as for the mechanical recycling of heterogeneous mixtures of plastics[1], with the goal of realizing sustainable multiphase polymeric materials with controlled morphology and properties.

Mechano-chemical treatments are based on the application of high shear and compressive stresses to solid materials, through, as an example, the action of planetary ball mills (ball mills, BM). Developed in the mining and metallurgical fields, these processes allow to obtain a fine grinding and the formation of alloys and metastable compounds. In organic materials, the BM treatment can induce structural/morphological changes (amorphization[2], intimate mixing of immiscible phases) but also chemical reactions, promoting the in situ formation of branching or even copolymerization through radical reactions. In lignocellulosic materials (e.g. agricultural waste), the treatment can deconstruct their fibrous structure allowing to separate the different fractions (micro and nano fibrils, nanocrystals) and to extract materials of interest.

The materials treated via ball mill will be characterized to evaluate the morphological and chemical variations produced by the process through the combination of different techniques. The analysis of the properties as well as of the property/structure relationships will not only support the optimization of the process conditions and the pre-competitive development, but will also allow to determine the most suitable application sectors.

Keywords

Circular Economy, Zero Waste, Mechanochemistry

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New Efficient Preparation of Polyfunctionalized Furans by Solid Supported Systems

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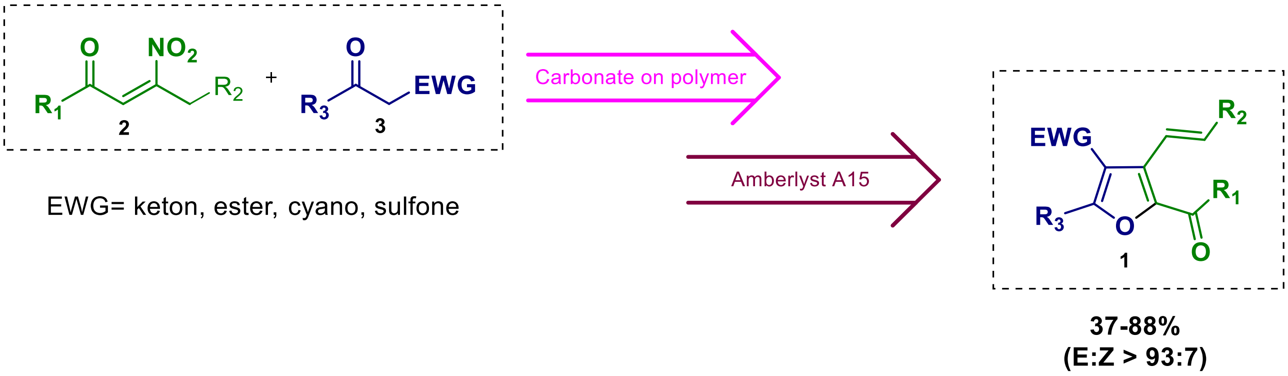
Abstract

Heterocyclic structures are ubiquitous and find huge application in pharmaceutical chemistry[1] and material sciences.[2] Among them, special attention has been given to five-membered heteroaromatic ring,[3] in particular, furans are important intermediate in the preparation of biologically active compounds.[4]

Herein, is presented a one-pot preparation of polyfunctionalized furans **1** starting from β-nitroenones **2** and active methylene compounds **3** (Scheme 1). The procedure involves two one-pot steps, both promoted by solid supported systems: *(i)* base-promoted Michael addition, followed by nitrous acid elimination and *(ii)* acid-catalyzed cyclization. Pure products **3** are obtained in good yields with excellent diastereoselectivity, moreover, thanks to the mild reaction conditions, several functionalities are tolerated.



Scheme 2.

Keywords: Heterocycles, One-pot, Solid Supported Systems.

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Reactivity of Ruthenium Acetylide Complexes Towards Carbon Dioxide

* * *

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Abstract

This research program aims to develop catalysts which can couple CO_2 to an inexpensive substrate to produce value-added products, an area in which there has been limited research. Previous research using phosphine complexes of iron has come close to developing a complete catalytic cycle for coupling CO_2 to acetylene (HC≡CH) to give propiolic acid (HC≡C(C=O)OH), using *trans*-$[FeH(C{\equiv}CH)(depe)_2]$.[1] A ruthenium-based catalyst, $[Ru(\eta^2\text{-}C_2H_4)(P(CH_2CH_2PPh_2)_3)]$, has been reported to couple CO_2 to ethylene ($CH_2{=}CH_2$) to give potassium acrylate ($KOC({=}O)CH{=}CH_2$) with a modest TON.[2]

The current program is investigating the reactivity of phosphine complexes of Ru towards CO_2 and acetylene. The cyclometalated complex $[RuH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3]$ reacts with HC≡CH, to give the metal acetylide complex *cis*-$[RuH(C{\equiv}CH)(PMe_3)_4]$, which reacts rapidly and completely with CO_2 to give $[Ru(OC({=}O)CH{=}CH\text{-}\kappa^2C,O)(PMe_3)_4]$. (Fig.1A-Step I) The complexes have been analysed by ^1H, $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ NMR (Fig.2B) spectroscopy, with further characterisation in progress. Reaction conditions are being investigated to cleave the metalalactone ring of $[Ru(OC({=}O)CH{=}CH\text{-}\kappa^2C,O)(PMe_3)_4]$, and release the propiolic acid fragment. (Fig.1A Steps II and III) *Cis*-$[RuH(C{\equiv}CH)(PMe_3)_4]$ also reacts with HC≡CH, to give the disubstituted complex $[Ru(C{\equiv}CH)_2(PMe_3)_4]$ as a minor biproduct.

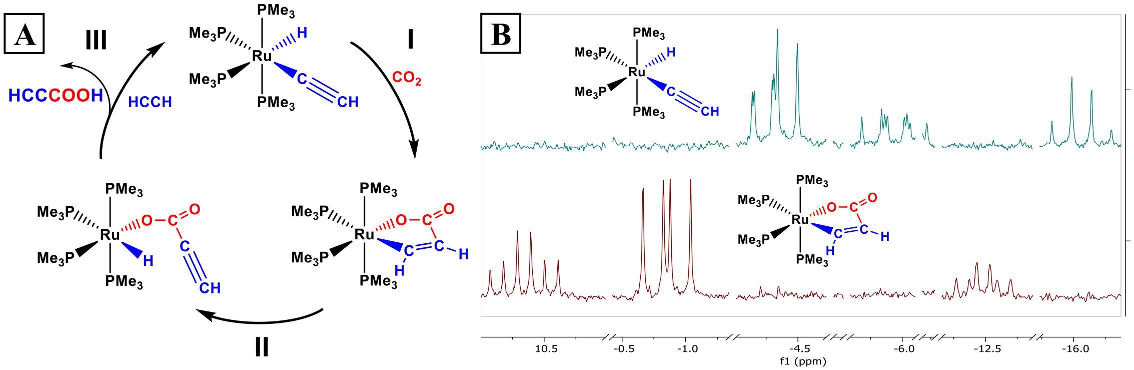

Figure 1. **A**. Proposed catalytic cycle. **B**. $^{31}P\{^1H\}$ NMR spectra for *cis*-$[RuH(C{\equiv}CH)(PMe_3)_4]$ (top) and $[Ru(OC({=}O)CH{=}CH\text{-}\kappa^2C,O)(PMe_3)_4]$ (bottom).

Keywords: catalyst, CO_2 coupling, acetylene, organometallic, phosphine, Ruthenium

Acknowledgements

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Direct Synthesis of Diphenylamines from Phenols and Ammonium Formate Catalyzed by Palladium

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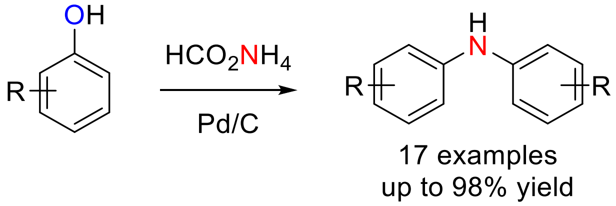
Abstract

Arylamines are commercially and synthetically useful compounds with a wide variety of applications, especially as antioxidizers and as synthetically relevant building-blocks. Their preparation has been traditionally achieved using metal-catalyzed C-N coupling reactions with aryl halides. However, we have found that using ammonium formate as the aminating reagent and phenol, with Pd/C as the catalyst, we are able to obtain symmetric diarylamines. Phenolic compounds are more desirable feedstocks due to their availability from lignin, making them valuable bio-renewable alternatives to aryl halides. Furthermore, this coupling reaction benefits from only generating water and CO_2 as by-products. Using this methodology we were able to synthesize 17 different diarylated amines from a convenient ammonia source using phenols as arylating reagents. Yields for the reaction ranged from good to excellent, except for severely sterically hindered substrates bearing multiple ortho substituents.



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Supporting information for this article is given via a link at the end of the document.

Investigating cyanogen rich *Manihot esculenta* efficacy for Ru phytomining and application in catalytic reactions

★★★

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Abstract

Increase in metals demand to produce metal-based products, has led to rise in prices for pure metal. In response, mining activities have increased thereby depleting most high-grade ore to leave abundant low-grade ores which are otherwise uneconomic to mine conventionally [1]. Therefore, there is a need to develop a cost-effective and eco-friendly phytomining technology using natural metal hyperaccumulator plants to extract the remaining valuable metals from low grade ores to produce a bio-ore [2]. The resulting bio-ore can then be used as a raw material for producing catalysts, for the chemicals manufacturing industry. Herein, we report the use of cyanogen rich *Manihot esculenta* in ruthenium phytomining to afford a bio-ore which was further processed into a plant-based catalyst, Ru@CassCat. The Ru@CassCat was fully characterized by TEM, EDX and applied in catalytic hydrogenation of furfural to furfural alcohol. Various test conditions were investigated such as temperature, pressure, effect of catalyst loading [3], and the results show that the catalyst is highly active at minimal load, giving very high turnover numbers. Therefore, these preliminary results mean that highly green biosynthesized nano-catalysts pose a promising and novel strategy to convert renewable feedstocks, like furfural, into high value end products that are a promising green source of biofuels to replace or augment fossil fuels. A generalized integration of processes from contamination to catalysis are shown in Figure 1.

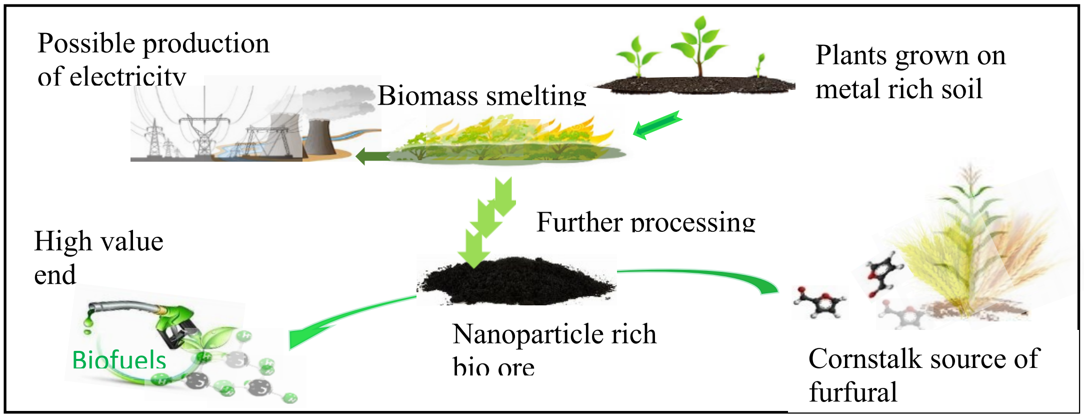

Figure 1: A general overview of a phytomining operation from planting to application of recovered metal nanoparticles

Keywords: *Manihot esculenta, ruthenium nanoparticles, catalysis*
Acknowledgements: National Research Foundation (NRF) South Africa, Research Centre for Synthesis and Catalysis, Department of Chemical Sciences, University of Johannesburg for funding.

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$CoFe_2O_4$-SiO_2-SO_3H magnetic nanocatalyst: An efficient catalyst for the synthesis of benzimidazoles and benzothiazoles

★★

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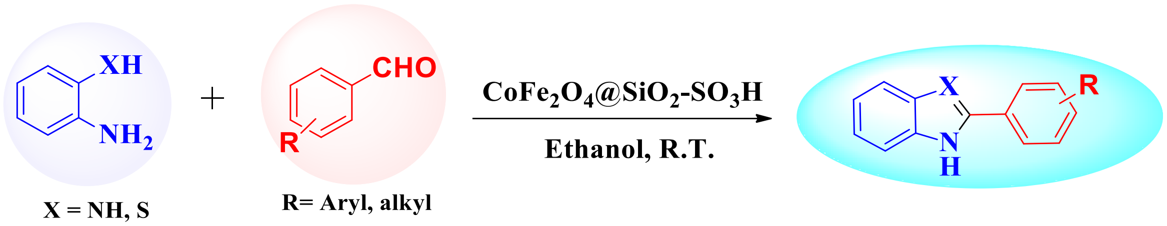
Abstract

A novel sulfonic acid functionalized cobalt ferrite magnetic nanocatalyst has been designed using cobalt ferrite as magnetic core. The synthesized nanocatalyst was characterized using various characterization techniques such as FT-IR, PXRD, FE-SEM, EDX, TEM, TGA, VSM and BET-SA. The magnetic nanocatalyst was employed for the synthesis of substituted benzimidazole and benzothiazole. Benzimidazole and benzothiazole were synthesized via condensation of *o*-phenylenediamine or 2-amino thiophenol with aldehydes in ethanol under room temperature. Upon completion of reaction catalyst could be easily recovered via. magnetic decanation or centrifugation and reused for several catalytic cycles without significant loss in their catalytic activity.

Tables and Figures



Scheme 1: $CoFe_2O_4$@SiO_2-SO_3H MNPs catalyzed synthesis of benzimidazoles and benzothiazoles

Keywords: Magnetic nanocatalyst, reusability, benzimidazoles and benzothiazoles

Acknowledgements

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Altering e-liquid composition and potential related hazards through the addition of water

* * *

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Abstract

Electronic cigarette refill liquids (e-liquids) are commonly composed of propylene glycol and glycerol as solvents, along with nicotine, an acid such as benzoic acid that protonates nicotine to create a nicotine salt, and a host of flavorants for aroma. One popular group of flavorants are flavor aldehydes such as vanillin, benzaldehyde, or cinnamaldehyde. As expected, these flavor aldehydes have been shown to react with the solvents propylene glycol and glycerol to form a variety of acetals in a simple mixture of the three components, without an active water removal step. Furthermore, acetals, such as vanillin propylene glycol acetal, have been detected in a wide variety of commercial e-liquids and a recent study has shown that flavor aldehyde propylene glycol acetals reach the aerosol and therefore the user's airways during "vaping" of the e-cigarette, and that they are relatively stable in the aqueous environment of the airways. Toxicological studies have shown that vanillin propylene glycol is in fact more irritating to human lung cells than vanillin itself and that benzaldehyde propylene glycol acetal is more toxic to BEAS-2B lung cells than pure benzaldehyde. Taken together, this raises several questions on e-cigarette safety as well as labeling requirements.

In an effort to reduce the buildup of flavor aldehyde propylene glycol acetals, this study explored the extent to which the addition of various amounts of water (0 wt-%, 5 wt-%, 10 wt-%, 20 wt-%) to a lab-made e-liquid suppressed the acetal formation therein. Initial results suggest that the equilibrium concentration between initially added flavor aldehyde and the corresponding acetal depends on the aldehyde. While for vanillin, the buildup reaches an equilibrium at an acetal mole fraction of ~0.5 in 3 weeks, benzaldehyde reacts much quicker and to an acetal mole fraction of up to 0.95. Since water is a by-product of the acetalization reaction, its addition is expected to reduce the total amount of acetal formed, and initial results confirm this: the addition of 20 wt-% of water can reduce the extent of flavor aldehyde acetal formation by a factor of up to 10.

E-liquid manufacturers could utilize this strategy to lower flavor aldehyde acetal contents in their products by using one of the most benign materials, water. In addition, water-containing e-liquids would also likely retaining the aroma profile since the free flavor aldehydes tend to have a stronger aroma than their corresponding acetals.

Acknowledgements

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Use POM anion-based ILs As High Performans Catalyst for Waste PET Alcoholysis

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Abstract

Polyethylene terephthalate (PET) has been widely used in many areas of our lives due to its excellent mechanical properties and chemical stability, but the large amount of consumption leaded to the accumulation of waste PET duo to its characteristics of degradation-resistant and then caused environmental pollution and waste of resources. Therefore, the recycling of waste PET is necessary and the related topics have also become research hotspot[1].

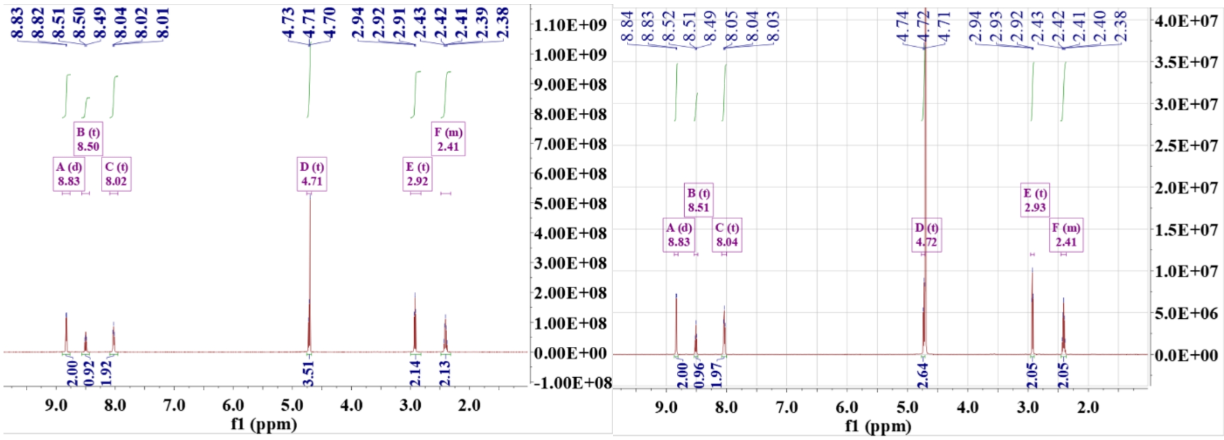
The catalyst plays an important role in the alcoholysis process of PET, and there have been many types of catalysts used in the alcoholysis of PET and achieved good results, such as metal oxides, solid acids, ionic liquids, and phase transfer catalysts. Among them, polyoxometalate (POM) is a special inorganic metal oxygen cluster, which has the advantages of high acidity, redox performance, good thermochemical stability, structural design and low toxicity. In this study, we combined organic cations with POM anions to improve the performance of the catalyst, which may be a new type of IL material[2]. We synthesized a kind of POM anion-based IL $[PyPs]_n[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$(n=3, 6, 9, 12) and investigated the performance of catalytic on PET alcoholysis. The PET could be completely degraded at 195 °C for 30 min, the amount of catalyst was 0.8% of PET mass, and the selectivity of bis(hydroxyethyl) terephthalate(BHET) reached more than 84%. The main degradation products were characterized by nuclear magnetic resonance spectroscopy (1H NMR), gel chromatography (GPC) differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM), and the reaction process of PET alcoholysis was studied by in situ infrared ray spectroscopy (in-situ IR).

Tables and Figures

Table 1. Catalytic activity of POM-ILs with different ratios

POM-IL	Conversion of PET(%)	Yield of BHET (%)	Time (min)
$[PyPs]_3[ZnW_9]$	100	84.46	45
$[PyPs]_6[ZnW_9]$	100	83.39	35
$[PyPs]_9[ZnW_9]$	100	81.24	50
$[PyPs]_{12}[ZnW_9]$	100	81.85	50

Reaction conditions: Temperature 195 °C; EG/PET/Cat=4:1:0.008



(a) (b)

Fig. 1 NMR spectra of PyPs(a) and [PyPs]$_6$[WZn$_3$(H$_2$O)$_2$(ZnW$_9$O$_{34}$)$_2$](b)

Keywords

POM-ILs, Catalyst, PET Alcoholysis

Acknowledgements

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Synthesis of NIPUs *via* thiol-ene polymerization of carbamates obtained from the Lossen rearrangement

★★★

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Abstract

Polyurethanes (PU) are one of the most important class of polymeric materials, with applications ranging from insulation panels and foams to high performance adhesives and fibres. Industrially, PUs are synthesized by polyaddition of isocyanates with diols. Isocyanates have been not only been confirmed to be toxic for humans, but are also produced using highly toxic phosgene and amines. An alternative procedure toward PUs is therefore of utmost importance.

In this work, we present a different approach, in which the urethane monomer is prepared *via* the Lossen rearrangement[1] in a one-step synthesis and polymerized with a dithiol to produce a polyurethane chain with thioether linkages. The advantage of this method lies not only in the sustainable design during the preparation of the carbamate functionality, but also in the tunability of polymer properties by choice of dithiol moiety and the employment of main side-products, the symmetrical urea, as a comonomer for the thiol-ene polymerization.

Keywords

Lossen rearrangement, non-isocyanate polyurethane, renewable resources

Acknowledgements

The authors would like to acknowledge support from the Karlsruhe Institute of Technology (KIT) and the Helmholtz Association.

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Iron functionalised hydroxyapatites as efficient eco-friendly catalysts for air-quality protection

★★★★

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Abstract

In the last decades, the ever more growing need of controlling the hazardous gaseous emissions into the air (including NO_x, N_2O and NH_3) moved researchers to the optimization of the current and most performant catalytic processes and related catalytic materials [1]. In this perspective, the central theme of our research is the development of efficient, low cost and eco-friendly catalysts for reactions of air-quality protection.

Among all the calcium phosphate materials, calcium hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) has emerged through the years as an interesting material in industrial and environmental catalysis due to its peculiar properties (e.g. high chemical and thermal stability, extremely low solubility, low cost, large availability, easy synthesis, modulable number of acid/base sites, and ion exchange capability) [2]. Recent studies have confirmed the possibility to obtain innovative multifunctional materials to be used as catalysts for environmental targeted reactions by functionalisation of HAP with different metal species (e.g. Cu, Fe, Mn). [3-5]

Herein we present our results on catalysts obtained from a commercial HAP (kindly supplied from Solvay) functionalised with Fe^{3+} towards some gaseous pollutant abatement reactions. A series of iron-modified samples (Fe/HAP_{IE}) with different metal loading ($2 <$ wt.% Fe < 13) has been prepared by ionic exchange procedure from iron(III) nitrate as precursor. A detailed study on Fe-speciation, acidity, morphology and structure has been realised through UV-DR and Mössbauer spectroscopies, NH_3 titration, N_2-physisorption and XRPD analyses.

In general, these samples possessed highly dispersed Fe^{3+} centers as predominant species, together with small amount ($\leq 15\%$) of Fe_2O_3 nanoclusters ($2 <$ size (nm) < 4), as revealed by UV-DR and Mössbauer spectroscopies.

The catalytic performances of Fe/HAP_{IE} samples have been evaluated in some environmental reactions: NH_3-SCR (catalytic reduction of NOx by NH_3), NH_3-SCO (catalytic oxidation of NH_3) and catalytic N_2O decomposition in a large temperature interval (from 120 to 800°C, depending on the reaction type) and at fixed GHSV (ca. 30000 h^{-1}). All Fe/HAP_{IE} samples were active in the studied reactions. As expected, differences in iron loading produced a diversified effect depending on the considered reaction. In particular, SCR activity strongly depended on Fe-amount, while no remarkable differences emerged in SCO and N_2O decomposition activity as a function of Fe loading.

Keywords Iron hydroxyapatite; De-NOx catalysts; Iron speciation.

Acknowledgements Dr. Sergio G. Marchetti from Cindeca, Centro de Investigación y Desarrollo en Procesos Cataliticos, La Plata, Argentina, is gratefully acknowledged for helping us in the interpretation of Mossbauer spectra. Authors acknowledge Solvay, Soda Ash and Derivatives, Rue de Ransbeek 310, Bruxelles, for supplying hydroxyapatite.

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Photodegradation of Textile Organic Dye waste using Biogenic Nitrogen-Phosphorous Codoped ZnO/CuO Nanocomposite

★★

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Abstract

Organic dyes are major pollutants and have become of paramount concern to the environmentalists. To treat them many conventional biological methods have been used. But these methods can't remove completely due to this heterogeneous Photocatalysis is used. Its advantage over the conventional methods is its low cost, highly efficient to remove the wastes completely, no production of secondary sludge, etc. So, the principal objective of this study was to investigate the removal of Methyl orange dye using N-P codoped ZnO/CuO nanocomposite. The photocatalyst was synthesized by the Co-precipitation method. Also, Rice, Chickpea, Soybean, and Sesame seeds have been employed as Nitrogen (N)–Phosphorous (P) precursors to synthesize the biogenic nanocomposite. Characterization of the crystal structure, functional groups, metal composition, and band gap energy of the composite was determined by using X-ray diffraction (XRD), Fourier transforms infrared (FTIR), Atomic absorption spectroscopy (AAS), and Uv-Vis spectrophotometric methods respectively in the presence or absence of the four crop seeds. Also, the photocatalytic activity of the naked and N-P codoped nanocomposite was investigated through the irradiation of Ultraviolet light. In this study, the degradation of model pollutant methyl orange dye was investigated through optimum degradation efficiency of 92.18% at 0.3g dose of the catalyst, 120min contact time, and pH of 8 respectively. The results show the Photodegradation efficiency of the doped samples has been a good result which confirms the positive effect of doping of biomasses through shifting of their absorption into visible lights for such applications. The doped photocatalyst had more efficiency than the naked photocatalyst and the Photodegradation efficiency was dependent on both concentration and pH parameters. In general, Photocatalysis has promising potential for the removal of organic toxic dyes such as methyl orange from aqueous solution to have a cleaned and green environment.

Keywords: Adsorption, Co-precipitation, Irradiation, Photocatalyst

Acknowledgements

In this study Arba Minch University is highly acknowledged for their material and financial support to complete this work.

Transition-Metal-Free Synthesis of Benzo[*c*]chromenes via Visible Light

★★★

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Abstract

6H-benzo[*c*]chromene ring is widely present in pharmaceutical and natural products.[1] For example, *Cannabinol* (Figure 1, **1**) is one of the most common cannabinoids and has an antimicrobial property.[2] Thus many different synthetic methodologies are known for the construction of benzochromenes. Pd, Co and Au have been used to obtain the benzochromene skeleton.[3–5] Moreover, a metal-free strategy has been developed to approach the desired ring using neocuproine-KO^{t}Bu complex in benzene at 100°C.[6] Due to the biological importance of benzo[*c*]chromenes, the development of an eco-friendly synthetic protocol that avoids the use of high temperatures, toxic solvents, ligands and even transition metals is still desired. Nowadays, the new application of visible light in organic synthesis pretends to replace the uses of ligands and high temperatures. Recently, it has been reported the use of iridium catalysts and visible light to initiate an intermolecular radical addition to biaryl vinyl ethers.[7]

It is known that homolytic aromatic substitution (HAS) reaction promoted by base and light efficiently works in intermolecular coupling reactions in biphenyls and stylbenes synthesis.[8,9] However, no heterocycle has been obtained by using this strategy. Herein, we demonstrate that 6H-benzo[*c*]chromenes can be easily obtained from the corresponding 2-halobenzylphenyl ether (Figure 1, **2**) and using blue light-emitting diode (LED) to promote the cyclization at room temperature.

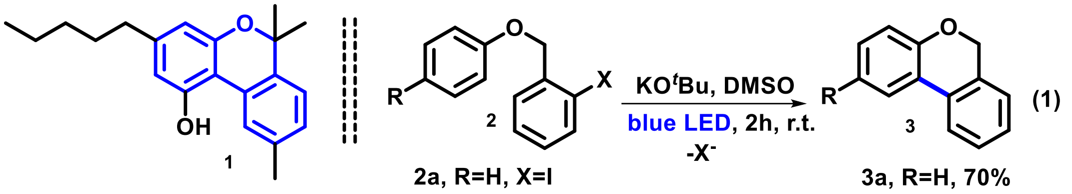

Figure 1. 6H-benzo[*c*]chromene ring in Cannabinol. Synthesis of 6H-benzo[*c*]chromene derivatives.

Keywords

Benzochromenes, Photochemistry, Visible Light

Acknowledgements

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A Novel Crystalline Azine-Linked 3D Covalent Organic Framework (COF) for CO_2 Capture and Conversion

★★★

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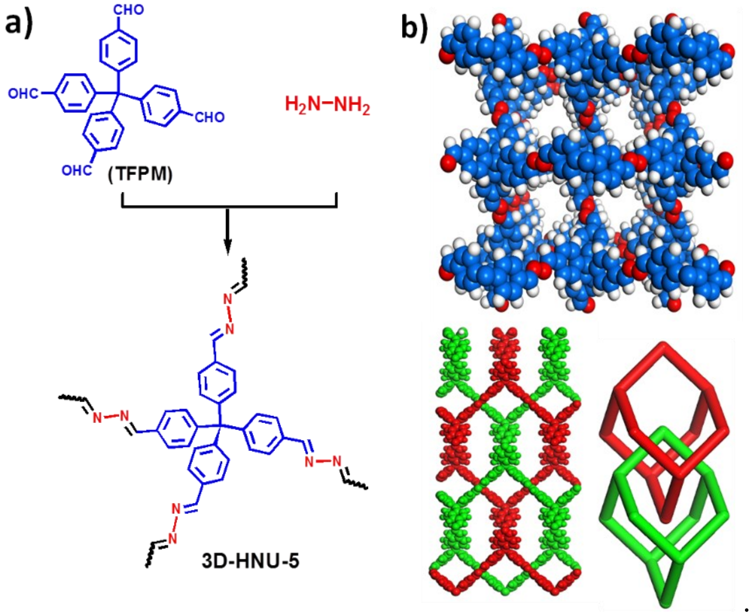
Abstract

The targeted synthesis of three-dimensional covalent organic frameworks (3D COFs) is a great challenge, especially that by using new kind of organic linkages. Herein, for the first time, a novel 3D azine-linked COF (3D-HNU5) has been synthesized and characterized. It is shown that the obtained 3D COF is a 2-fold interpenetrated diamond topology, and shows good chemical / thermal stability and a narrow pore size distribution, which features excellent performance in selective uptake of CO_2 over N_2. Moreover, the 3D-HNU5 is found to be an efficient catalyst to catalyze the cycloaddition of propargylic alcohols with CO_2 into carbonates with excellent catalytic activity under mild conditions.

Tables and Figures



Scheme1. Schematic representation for the synthesis of the azine-linked 3D-COF (a), and its 3D porous structure and 2-fold interpenetrated diamond topology (b).

Keywords: 3D COFs, selective uptake of CO_2/N_2, CO_2 cycloaddition

Acknowledgements

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Unveiling the mechanism of pathway-tunable aliphatic carbonate synthesis from incorporated CO_2 adducts by tracing oxygen isotopes

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Abstract

The capture and conversion of CO_2 has been receiving close attention for environment protection. The conversion of CO_2 to value-added chemicals, such as aliphatic carbonates, offers an opportunity for CO_2 utilization. Due to the chemical inertness of CO_2, catalysts have been prepared to reduce activation energy [1], and process intensification was developed for shift of chemical equilibrium to enhance product yield [2]. However, considerable energy cost is required to activate CO_2 and accelerate the synthesis of aliphatic carbonates.

We developed a two-step strategy for pathway-tunable conversion of CO_2 to aliphatic carbonates under ambient conditions. With CO_2 captured and activated in 1-alkyl-3-methylimidazolium CO_2-adducts (C_mC_1Im-CO_2), we focused on the aliphatic carbonate synthesis from C_mC_1Im-CO_2 and alcohols in haloalkanes, where the exemplified system produces dimethyl carbonate (DMC) with high selectivity of 99.9% at CO_2 conversion of 40.2%. Isotopic labelling experiments validated our proposed reaction mechanism and we further interpreted the tunable reaction pathways for aliphatic carbonate synthesis by NMR characterization and theoretical calculations.

Hydroxides (MOH) and alkaline salts (MAn') were used to prepare 1-alkyl-3-methylimidazolium ILs ($[C_mC_1Im][An]$) with $[C_mC_1Im][Br]$. C_mC_1Im-CO_2 was formed in CO_2-treated $[C_mC_1Im][An]$ with CO_2 absorption capacity and contents measured by a pressure drop method. With the addition of alcohols and haloalkanes (RX_n), aliphatic carbonates were tuned to be synthesized in different reaction pathways under ambient conditions. The sample was injected into Agilent 7890 GC equipped with a flame ionization detector and a HP-PLOT/Q column ($30\ m \times 0.53\ mm \times 40\ \mu m$) for product analysis. ^{18}O isotopic labelling of methanol was analyzed in Agilent 7890A-5975C GC-MS equipped with a flame ionization detector and an electron impact ion source and ^{13}C NMR spectra were recorded at 23 °C on a Bruker Avance Ⅲ 100 MHz spectrometer. σ-Profile analysis was based on COSMO-RS theory and DFT calculation was performed with B3LYP functional at the 6-31++G** theoretical level in Gaussian 09.

$[C_2C_1Im][OAc]$ captures 7.8 wt% CO_2 and activates CO_2 by altering its hybridization from C(sp) to C(sp^2) through C_2C_1Im-CO_2 formation [3]. When methanol is used as alcohol substrate, DMC yield of 9.4% and 2.6% with selectivity of 99.7% and 99.8% are obtained in CH_3I and CH_2I_2, respectively (Table 1). By altering $[C_mC_1Im][An]$, the highest CO_2 conversion can reach 40.2% with 99.9% selectivity to DMC. we are also able to extend the range of alcohol substrates for production of aliphatic carbonates under ambient conditions. ^{18}O isotopic labelling of methanol validates our proposed tunable reaction pathways for aliphatic carbonate synthesis. ^{13}C NMR characterization, σ-Profile analysis, and DFT calculation are performed to study the pathway-tunable conversion of CO_2. It shows that alcohols are nucleophiles and alkoxylation reagents while haloalkanes serve as buffers, solvents, and alkylation reagents. The developed two-step strategy is promising in converting CO_2 to value-added products under ambient conditions, which provides alternative perspectives for CO_2 capture and utilization (Fig. 1).

Table 1. CO_2-based yield and selectivity of DMC synthesized from CO_2-treated imidazolium acetates under ambient conditions.

Entry	CO_2-treated IL	RX_n	Yield (%)	Selectivity (%)
1	$[C_2C_1Im][OAc]$	CH_3I	9.4	99.7
2	$[C_2C_1Im][OAc]$	CH_2I_2	2.6	99.8

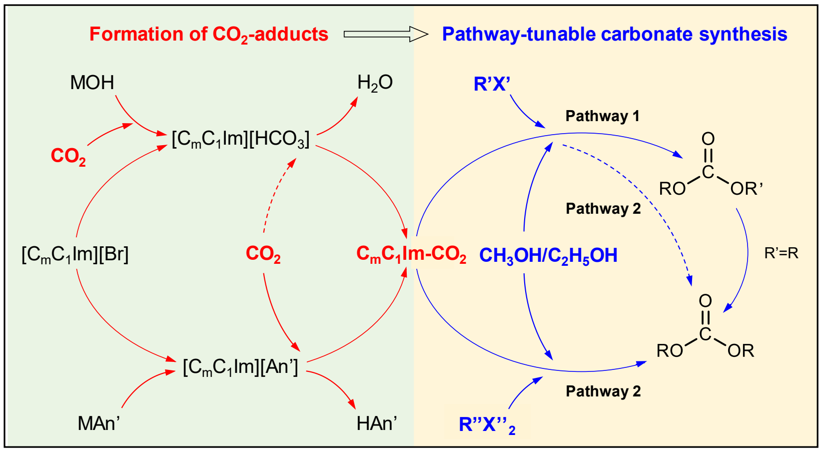

Figure 1. A two-step strategy for pathway-tunable conversion of CO_2 to aliphatic carbonates under ambient conditions.

Keywords

Pathway-tunable mechanism; CO_2 conversion; aliphatic carbonate; ionic liquid; oxygen isotope

Acknowledgements

The financial support from National Natural Science Foundation of China (21576081 and 21776074) is greatly acknowledged.

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Procognitive and antidepressant activity of novel anilide derivative with 5-HT$_{1A}$/5-HT$_7$ receptor antagonistic properties and PDE4/7 inhibitory activity

★★★

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Abstract:

Cognitive and mood disorders are a growing health, social, and economic issue as they often co-occur and accompany various forms of dementia, depression, and schizophrenia. They are clinically relevant features in Alzheimer's disease which is one of the most prevalent age-related neurodegenerative diseases and whose treatment options are currently limited. There is an urgent need to develop novel drugs that will be able to effectively reduce cognitive and mood disorders. According to latest literature data, such multidirectional activity may be achieved by combining the interaction with serotonin 5-HT$_{1A}$ and 5-HT$_7$ receptors and inhibition of cyclic-3′,5′-adenosine monophosphate (cAMP)-specific phosphodiesterase (PDE) 4 and 7 [1,2].

The aim of this study was to evaluate procognitive and antidepressant activity of selected 5-HT$_{1A}$/5-HT$_7$ receptor antagonist with additional PDE4/7 inhibitory activity using animals behavioural tests.

The procognitive and antidepressant activity was tested in Wistar rats using well-established experimental paradigms, *i.e.*, novel object recognition and forced swimming tests, respectively. Moreover, in order to exclude the possibility of competing behaviors such as general locomotor activity, the open field test was carried out and the influence of effective doses was studied.

Tested compound at a dose of 3 mg/kg (*i.p.*) significantly reversed MK-801-induced episodic memory deficits in the novel object recognition test, while at a dose of 10 mg/kg (*i.p.*) reduced the immobility time of animals (by about 34%) in the forced swimming test. The antidepressant-like effect produced by tested compound was stronger than that of escitalopram used as a reference drug. This study opens a new perspective in the search for an efficacious drug for the treatment of cognitive and depressive disorders.

Keywords: procognitive and antidepressant activity; multifunctional ligand; 5-HT$_{1A}$/5-HT$_7$ receptor antagonist and PDE4/7 inhibitor.

Acknowledgements:

This study was supported by the National Science Centre, Poland (Grant No. 2017/25/N/NZ7/00544).

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Selective Hydrogenation of Fluoroaromatics using Rh Nanoparticles Immobilized on Functionalized Silica Supports

★★★

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Abstract

Fluorinated cycloalkanes are exploited as key building blocks in the production of pharmaceuticals, fine chemicals [1], *etc.* A straightforward approach for their production consists in the hydrogenation of fluoroaromatics. However, this pathway has been scarcely studied with heterogeneous catalysts due to competing hydrodefluorination [2-3]. In the present work, this challenge was taken up by developing catalytic systems based on Rh nanoparticles immobilized on silica-based supports [4]. The influence of both the catalysts physico-chemical properties and the experimental conditions on the hydrogenation/hydrodefluorination selectivity were investigated to identify the most suitable catalytic system.

Using specifically designed catalyst and optimized conditions, a scope of fluorinated cyclohexane derivatives with different functionalities could be synthesized in high yields. In addition, efficient recycling experiments were carried out on the catalyst confirming its activity and stability in repeated cycles.

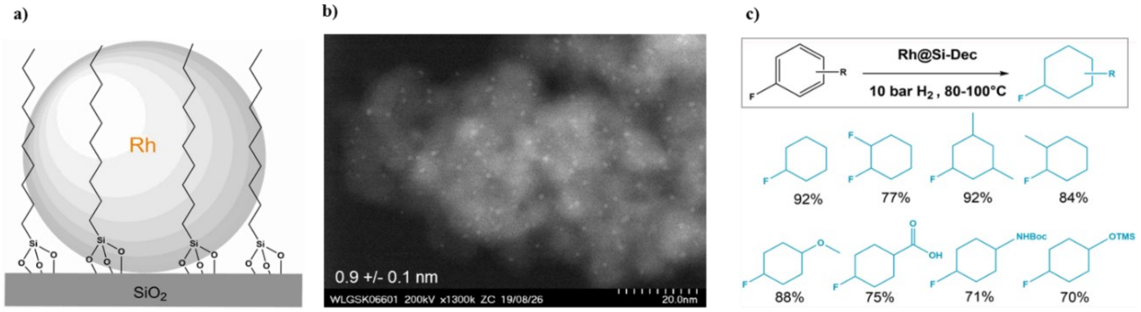

Figure 3: Hydrogenation of fluoroaromatics using a Rh@Si-Dec catalyst. a) Illustration; b) Scanning Transmission Electron Microscopy with High Angle Annular Dark Field (STEM-HAADF) picture; c) Catalytic results.

Keywords

Selective hydrogenation; fluoroaromatics; rhodium nanoparticles; functionalized silica supports.

Acknowledgements

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Searching for potential antibiotic adjuvants in the group of 5-(fluorobenzylidene)imidazolones

★★★

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Abstract

Antibiotics were discovered in XX century and it was a great breakthrough in the treatment of bacterial infections. Unfortunately, after a few years, lack of response was observed for antibacterial drugs, which were previously effective. This phenomenon is called drug resistance. Currently, multidrug resistance (MDR) is a serious, global problem in many diseases, *e.g.* bacterial infections. For this reason, searching for solution to overcome bacterial MDR is crucial. One of the approaches is a search for antibiotic adjuvants. These compounds are able to block at least one of mechanisms of MDR, *e.g.* enzymes, efflux pumps, without intrinsic antibacterial activity [1,2]. Compounds with such activity were found in the group of 5-arylideneimidazolones with amine moiety at position 2 and alkylamine at position 3 [3]. Therefore, the aim of this research was synthesis and microbiological assays for new potential antibiotic adjuvants in the group of 5-(fluorobenzylidene)imidazolones. A series of six new compounds was designed based on the previously found active compounds [3]. Final products were synthesized in four stages *i.e.* (i) Knoevenagel condensation, (ii) S-methylation, (iii) reaction with amine, (iv) Dimroth rearrangement. Obtained compounds were tested in three *S. aureus* (Gram positive) bacteria strains, reference (ATCC 25923) and MDR (MRSA 19415 and 19449). Firstly, antibacterial activity assay was carried out in order to evalute intrinsic MIC. Then, their ability to increase oxacillin efficacy was investigated. The best compound found caused a significant (4-fold) reduction of the antibiotic MIC in MRSA 19449 strain. To sum up, these studies indicated that the imidazaolones with fluorobenzylidene substituents could be potential antibiotic adjuvants. Nevertheless, further studies in other bacterial strains and with various antibiotics are needed.

Keywords

5-Arylideneimidazolones, antibiotic adjuvant, *S. aureus*

Acknowledgements

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Amine-Responsive Disassembly of Au^{I}–Cu^{I} Double Salts for Oxidative Carbonylation

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Abstract

A sensitive amine-responsive disassembly of self-assembled Au^{I}-Cu^{I} double salts was observed and its utilization for the synergistic catalysis was enlightened. Investigation of the disassembly of [Au(NHC)$_2$][CuI$_2$] revealed the contribution of Cu-assisted ligand exchange of N-heterocyclic carbene (NHC) by amine in [Au(NHC)$_2$]$^+$ and the capacity of [CuI$_2$]$^-$ on the oxidative step. By integrating the implicative information coded in the responsive behavior and inherent catalytic functions of d^{10} metal complexes, a catalyst for the oxidative carbonylation of amines was developed. The advantages of this method were clearly reflected on mild reaction conditions and the significantly expanded scope (51 examples); both primary and steric secondary amines can be employed as substrates. The cooperative reactivity from Au and Cu centers, as an indispensable prerequisite for the excellent catalytic performance, was validated in the synthesis of (un)symmetric ureas and carbamates.

Keywords Cabarmats ； double salts ； oxidative carbonylation; synergistic catalysis; urea

Acknowledgements

The work was supported by NSFC (91645118, 21633013, 21802151, 21703159) and NSF of Jiangsu Province (BK20180249). L.H. thanked Key Research Program of Frontier Sciences of CAS (QYZDJ-SSW-SLH051). Y.C. acknowledged the grant from the Strategic Priority Research Program of CAS (XDB17000000) and CAS-Croucher Funding Scheme for Joint Laboratories. Ms. Ying Ma was acknowledged for HRMS. Thanks go to Profs. Aiwen Lei, Fuwei Li and Senmiao Xu for sharing equipment. XAS was conducted at beamline TLS-17C1 of NSRRC in Hsinchu and BL14W1 of SSRF in Shanghai.

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Critical mineral extraction and separation by intensified Solvent Extraction (SX), Ion Exchange (IX) and Molecular Recognition Technology (MRT)

★

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Abstract

There is an increasing demand for environmentally safe metal extraction separation procedures. The outlook for rare earth elements (REE) market shows that the demand for selected members of the REE family is expected to grow in the coming decades. This is driven by the global population increase, increased wealth, need to replace end-of-life products containing REE, and production of new products containing REE. For instance, the demand for NdFeB magnets in end-use products, such as windmills, electric motors, electric bikes, and external hard disk drives will increase significantly. Also, total rare earth oxide (TREO) demand will be ramped up after 2025 compared to the 2020-2025 time frame, as many emerging technologies requiring REE are poised to grow rapidly.

The extraction of REEs is mainly based on traditional solvent extraction procedures, which are low in metal selectivity and high in waste generation and capital/operating expenses. Intensified extraction, in particular microwave-assisted solvent extraction (SX), as well as separation technologies such as ion extraction (IX) and molecular recognition technology (MRT) are all greener technologies that either require no or less organic solvents, generate minimal waste while being routinely scalable with reduced energy needs, highly selective in metal separation and cost-effective[1].

The separation of selected individual REE using MRT provides a platform for maximum value-added in end-use markets. High selectivity, coupled with the elimination of organic solvents, results in a clean, efficient separations process that can be applied to numerous feed sources and can produce purified REE for introduction directly into the manufacturing chain of a variety of end-use products. This type of system can be constructed and put into place in service developing REE mines and target operations with high TREO from process operations and tailings. Green chemistry will promote sustainability at the molecular level. Canada will greatly benefit from the techno-economic success of this project by implementing on its territory a clean technology for REE recovery. A clean technology also brings inevitably environmental and social benefits as improving the quality of the environment translated into improving life quality as well.

This research project tackles the valorization of mining industry tailings and residues, namely iron-rich tailings derived from REE extractions and asbestos residues, which we will accomplish with green extraction and separation methods. The general objective of this project is to implement an integrated system for the efficient extraction, recovery and separation of target metals from ore extraction tailings at the pilot scale by respecting the green chemistry principles[2]. There are two matrices that we will target: i) one matrix containing big quantities of iron (over 50%), Co, V, Cr, Ni, Sc and probably two other critical rare earth elements; ii) another sample with Fe (over 30%), Ti, V, Cr, Sc and where the leaching media is HCl.

Keywords

Mineral tailings, extractive metallurgy, metal recovery, mineral residue, green processing, process intensification, MRT, REE

Acknowledgements

The authors would like to express their gratitude to the MITACS for the financial support and IGS Inc. for providing the equipment for design and construction of experimental set-up.

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Synthesizing Particular Metal Coordination Precursor for Nano Solid Electrolyte Preparation Toward to Its Unprecedented Bio-application to Inhibit the Biofilm Formation

★

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Abstract

In recent years, the classical and modern coordination chemistry has gained much attention in the study of the metal coordination complexes of various applications in the fields of both bio-inorganic chemistry and advanced material science[1-3].
As a result of this view, we are noticing that synthesizing particular metal coordination precursors *via* the green chemistry method is a very challenging task in this field.My present research interest is established that I am able to synthesize particular precursors as a vital role in the biochemical reactions and apply them for the production of metal oxide nanoparticles.

In this present abstract, I will have been mainly focusing on the preparation of some precursors such as Ba(mdea) and Zr(mdea) by the method of green synthesis. And then, these precursors will be mixed and further calcined to fabricate the Y-doped $BaZrO_3$ (BZY) nanoparticle as a solid electrolyte with a feature in proton conduction.

I will collaborate with Dr.Wei Peng Li, who has developed many novel nano-materials and applied them in various bio-applications[4-5]. In the nearer future, we will use both of our coordination chemistry and chemical biology knowledge in the further studies.

Acknowledgements: We are so thankful to our affiliations.

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Key words: Inorganic Synthesis, Coordination Chemistry, Sol-gel, Metal oxide Nanoparticles and Solid Electrolyte.

Fixation of CO_2 into cyclic carbonates catalyzed by heterogeneous DBU based supported ionic liquid catalyst

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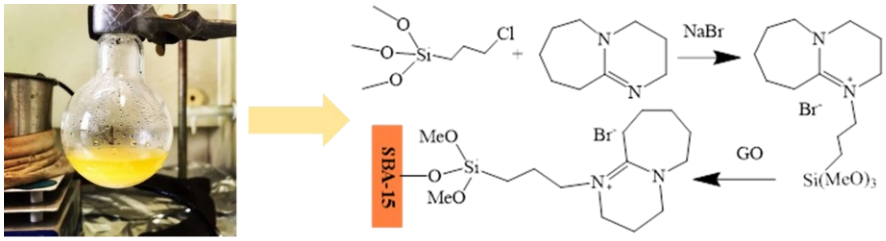
Abstract

CO_2 emission has caused environmental problems all over the world. The fixation of CO_2 into cyclic carbonates is an effective way of utilizing CO_2. On account of the unique properties different from the traditional catalysts such as designability, eco-friendly, etc., ionic liquid catalysts (ILCs) have shown great potential in the CO_2 cycloaddition reaction.[1] To obtain efficient and eco-friendly catalysts that could be separated facilely, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) base ILs has been synthesized and immobilized onto the internal pore surface of SBA-15 via silane coupling agent as a bridge to prepare supported ionic liquid catalysts (SILCs). Halogen were introduced as the anions to improve the catalytic activity. As expected, the prepared SILCs showed great performance (epichlorohydrin conversion >90%) in catalyzing the synthesis of cyclic carbonates via CO_2 cycloaddition with epoxides under condition: 80 °C, 2 MPa of CO_2, 12 h.

Tables and Figures



Preparation process of DBU@SBA-15

Keywords

Ionic liquid catalysts; CO_2 fixation; supported ionic liquids

Acknowledgements

We gratefully acknowledge the National Natural Science Foundation of China (Grant No. 21978043, U1662130) for financially supporting this research.

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Hypervalent Iodine reagents for Sulfonyl-transfer reactions

★★★

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Abstract

The presence of sulfonamides in medicinal agents is widespread. Many pharmaceuticals prescribed either bear a sulfonamide subunit or are co-administrated with a sulfonamide-containing drug.1 Currently, the most common way to prepare sulfonamides is with sulfonyl-chlorides, which are unstable and hard to handle compounds, and are generally created via the use of chlorosulfuric acid2 or thionyl chloride,3 both being highly toxic and corrosive compounds. In addition, sulfonylation reactions with SO2 surrogates, such as DABSO, remain incompatible with amines.3

Hypervalent Iodine Reagents consist of compounds containing iodine in a higher oxidation state, generally iodine(III) or iodine(V). While iodine(V) compounds are typically oxidation reagents, e.g.: Dess-Martin periodinane,4 iodine(III) compounds exhibit reactivity and chemical properties similar to those of transition metal complexes,5,6 acting as electrophilic synthons of normally nucleophilic groups.7 Benziodoxoles and benziodoxolones are cyclic compounds containing a iodine(III) core, which have attracted much interest in the scientific community due to their increased stability when compared to the acyclic analogues.8 In this presentation, benziodoxolone-derived reagents are disclosed in sulfur-atom transfer reaction for the sulfonylation of amines and anilines (**Scheme 1**).9 The versatility of the method and reaction scope will be presented.

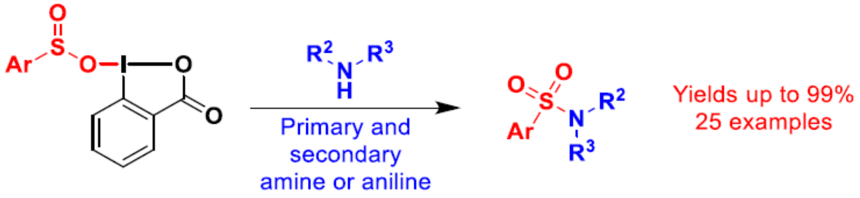

Figure 1 – Sulfonamide synthesis using our hypervalent iodine reagent.

Acknowledgments: We thank the FC&T for fellowships PD/BD/142864/2018 and SFRH/BD/116322/2016. This work was supported by the Associate Laboratory for Green Chemistry- LAQV which is financed by national funds from FCT/MCTES (UID/QUI/50006/2019) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265). The National NMR Facility is supported by FC&T (ROTEIRO/0031/2013 – PINFRA/22161/2016, co-financed by FEDER through COMPETE 2020, POCI, and PORL and FC&T through PIDDAC).

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Inorganic-Perovskite Catalyzed Transfer Hydrogenation Reaction of Cinnamaldehyde Using Glycerol as a Hydrogen Donor

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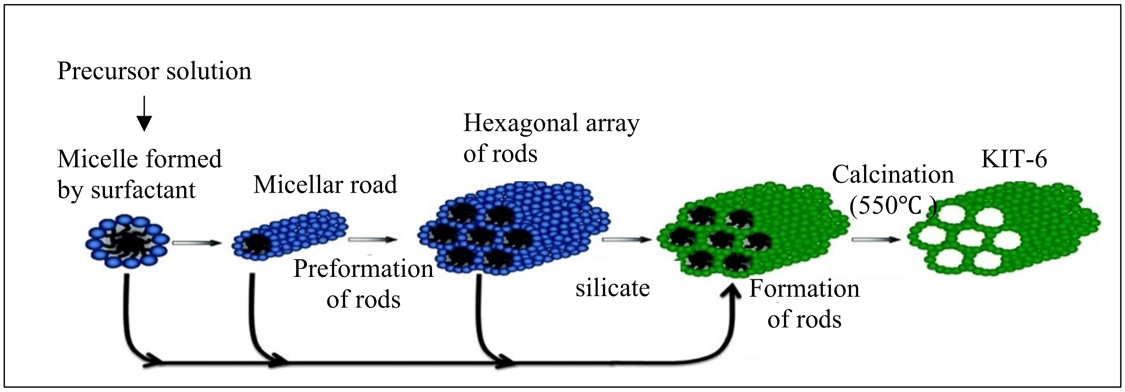
Abstract

Catalytic transfer hydrogen reactions (CTHs) produce value-added chemicals in the most economic, safe, sustainable, and green way [1]. This reaction uses renewable bioderived materials as hydrogen donors instead of the highly flammable and difficult to transport molecular hydrogen [2]. Herein, glycerol which is produced as a waste material during biodiesel production is used as a hydrogen donor to reduce the use of solvents for the reaction. Furthermore, the study aims in the hydrogenation of cinnamaldehyde into cinnamyl alcohol using SnO_2, $LaFeO_3$ and $LaSnO_3$ catalysts. The catalysts were synthesized through the nanocasting (hard template) method with SiO_2 (KIT-6) as a template. The template was synthesized using the sol gel method as illustrated in Scheme 1, resulting in high N_2-BET surface areas of 625 m^2/g and 135 m^2/g for the perovskites. As-synthesized catalysts were further characterized using p-XRD, H_2-TPR, TGA, TEM, SEM-EDX prior to catalytic evaluations. From GC-FID results, high conversions were obtained for cinnamaldehyde up to 99% and selectivity up to 87%. Concisely, the reaction was proven to be a surface reaction with the catalytic activity owed to the acidity and/or reducibility of the catalyst together with surface properties.



Scheme 1 :Synthesis of KIT-6 using the soft template method [3,4].

Keywords: Catalytic transfer hydrogenation, glycerol, perovskites,

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Catalytic hydrogenation of CO_2 via porous-silica-supported Au nanoparticles in aqueous solutions

★★★

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Abstract

The hydrogenation of CO_2 to C1 products with an 80% yield in water is reported using porous-silica-supported Au nanoparticles (Au/SiO_2) as catalysts. This catalytic reduction was performed in the absence of an organic solvent, and the catalyst is easily recycled. A reusability test shows no significant decrease in catalytic activity after four cycles. The reaction process starts with the capture of CO_2 by aqueous amines to form bicarbonates and carbamates. The subsequent hydrogenation is undertaken in the presence of an Au/SiO_2 catalyst at moderate temperatures and pressures in water. With Lewis acid additives, the Au/SiO_2 catalyst enables an efficient conversion of CO_2 to methanol, formate, amongst hydrocarbon derivatives. A mechanistic study reveals two different pathways for methanol production in the catalytic process: the direct hydrogenation of formate, and an indirect pathway via formamide.

Tables and Figures (optional)

Keywords

CO_2 hydrogenation, Au(0) catalysts, heterogenous catalysis, methanol, formic acid

Acknowledgements

The authors would like to thank Dr. Xue-Dong Liu (FEMR, McGill) for the TEM imaging, Dr. Robin Stein (McGill Chemistry Characterization Facility) and Dr. Tara Sprules (Quebec/Eastern Canada High Field NMR Facility) for the assistance in quantitative ^{13}C NMR. Funding: This work was supported by Natural Sciences and Engineering Research Council (NSERC) and by Fonds Québécois de la Recherche sur la Nature et les Technologies (FQRNT).

Understanding the mechanism of Ir^{III} And Pd^{II} catalyzed CO_2 hydrogenation in water

★★

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Abstract

CO_2, which is one of the greenhouse gases emitted mainly from burning fossil fuels, is major threat to the environment and is believed to be the cause of global warming. However, by hydrogenating CO_2 to various products such as methanol and dimethyl ether, it can be used as a cheap and non-toxic C1 source. In addition, hydrogenating CO_2 serves as a means of H_2 storage in the form of liquid energy carriers such as formic acid, methanol and dimethyl ether.[1-3] Various iridium(III) and palladium(II) complexes that posses, rigid, electron-rich and bulky ligands have served as efficient catalysts for carrying out various CO_2 transformations.[4,5] Herein we report the synthesis of a series of N^N bidentate tetrazolyl ligands and their corresponding palladium(II) and iridium(III) complexes (**Figure 1**). These complexes served as excellent pre-catalysts for the CO_2 hydrogenation at relatively low catalyst loadings *via* molecular catalysis. *In situ* ^{1}HNMR experiments demonstrate the formation of a catalytically active iridium-hydride specie through initial generation of a bridged Ir···H···Ir intermediate. Subsequently, the reaction proceeds by direct CO_2 hydrogenation or pre-formed $NaHCO_3$ reduction with likely intermediates being observed experimentally.

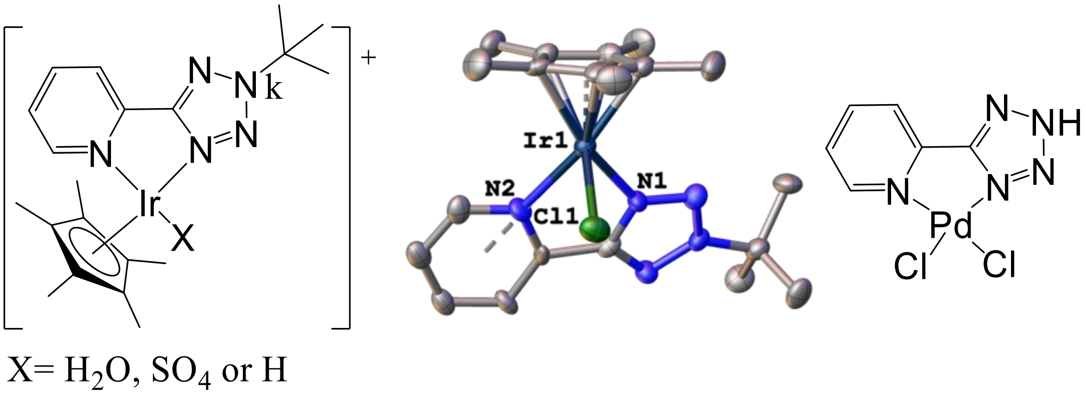

Figure 1: CO_2 Hydrogenation using Iridium and Palladium tetrazolyl complexes

Keywords: tetrazolylpyridyl, palladium(II) complexes, iridium(III) complexes, CO_2 hydrogenation, $NaHCO_3$ reduction

Acknowledments: UJ, Department of Chemical Sciences, NRF South Africa

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Highly Efficient Visible Light-Driven Rhenium Catalysis for CO_2 Reduction through Second-Sphere-Modification Strategy

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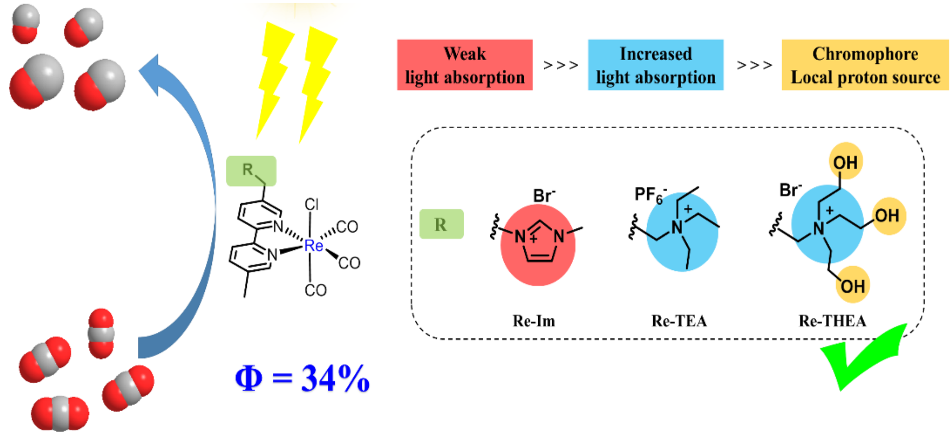
Abstract

Designing catalyst for CO_2 reduction into CO by harnessing sunlight is a promising project. We present here a facile strategy to design of ionic secondary coordination sphere modified Re catalyst for photo-reduction of CO_2 to CO by visible light. By adding ionic liquids or tuning different ionic secondary coordination sphere, we discover outstanding optical property, other than CO_2 absorption ability or the ability to dissociation of chloride anion, is the prerequisite for catalyst designing. Comparing with traditional $Re(bpy)(CO)_3Cl$ complex, the Re catalyst exhibits higher efficiency and stability after featuring tris(2-hydroxyethyl)amine (THEA) group on the secondary coordination sphere， thus resulting in a relative high quantum yield (up to 34%) for visible light-induced CO_2 reduction with single-molecule system. By the combination of experimental results and DFT calculations, the pendent ionic THEA group on Re-THEA, is found to enhance visible light absorbance, stabilize reaction intermediates and suppress the Re-Re dimer formation.



Scheme 1. Catalyst designing strategy: optimizing ionic second coordination sphere on Re complexes in photocatalytic CO_2 reduction reaction

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Reaction Pathways of Green Synthesis of SnO_2 Nanoparticles by Chemical Precipitation Method towards Practical Application

★★

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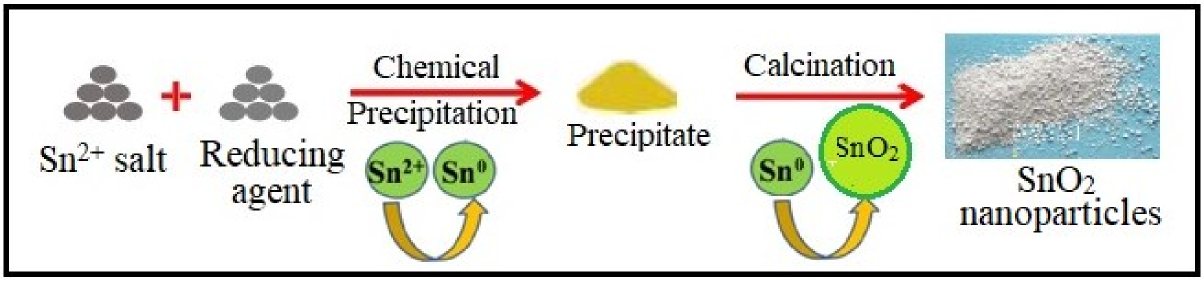
Abstract

Tin oxide (SnO_2) with versatile properties is of substantial standing for practical application and improved features of the material is demonstrated in the current issue through integration of nanotechnology with bio-resources termed as green synthesis of SnO_2 nanoparticles (NPs). This manuscript reveals the recent advances in green synthesis of SnO2 NPs by chemical precipitation method focused on distinct methodologies, characterization and bio–reduction mechanism of the synthesis along with photocatalytic application for dye degradation. The chemical precipitation method is more attractive due to fast reaction kinetics, cost-effective, chemical homogeneity and amazing crystal qualities. Numerous bio-based precursors selectively extracted from biological substrates have effectively been applied as capping or reducing agents to achieve the metal oxide NPs [1]. The major precursor obtained from the aqueous extract of *Catunaregam spinosa* root barks is found to be *7–Hydroxy–6–methoxy–2H–chromen–2–one* that has been proposed as a model compound for the reduction of metal ions into nanoparticles due to having highly active functional groups, eco-friendly, abundant in plants (67 wt%) and easy to extract. This work also describes the advances on the understanding of the bio-reduction pathways of the synthesis.



Scheme 1: Schematic presentation of chemical precipitation method for the preparation of SnO_2 NPs by a reducing agent.

In addition, photocatalytic activity of SnO_2 NPs for dye degradation has been discussed in the context with promising reaction mechanism and their properties exclusively depend upon a number of factors, e.g., particle size, band gap, crystal defects, dosage of the catalysts, etc [2]. It can be concluded that SnO_2 NPs could be a potential photocatalyst against degradation of industrial effluents.

Keywords: Nanotechnology, SnO_2, Green synthesis, Precipitation method, Application.
Acknowledgements: The authors acknowledge the joint contributions of Jashore University of Science and Technology and University Malaysia Pahang.

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Cyclodextrin nanosponge formulations for the treatment of COVID-19

★★★

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Abstract:

The coronavirus disease 2019 (COVID-19), appeared in December 2019, has spread rapidly, with many cases now confirmed worldwide. Scientists are currently trying to to discover drugs and efficacious therapies for the treatment of the viral infection. Chloroquine phosphate, a well-known drug for the treatment of malaria, has shown marked efficacy in treating COVID-19. The aim of this study is to boost the antiviral effect of chloroquine phosphate by encapsulating it in cyclodextrin (CD) nanosponges (NSs).

CDNSs are insoluble polymers obtained by reacting cyclodextrin with a crosslinking agent. In this work, β-CD was crosslinked with 1,1'-carbonyldiimidazole (CDI) and pyromellitic dianhydride(PMDA) in different molar ratios. The ability of both CDI and PMDA NSs to encapsulate chloroquine was investigated and compared. Preliminary results indicate a good affinity between chloroquine and the negatively charged polymer structure of the PMDA NSs. While the use of CDI NSs resulted in lower encapsulation efficiency. Quantification of chloroquine extracted from the loaded NSs was assessed by HPLC analysis. Then, chloroquine-loaded NSs were studied using several characterization techniques, including CHNS elemental analysis, thermogravimetric analysis and Fourier transform infrared analysis.

Keywords: COVID-19, β-CD NS, Chloroquine phosphate

Eco-Friendly Ball Mill Synthesis of Cyclodextrin Crosslinked Biopolymers

★★★

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Abstract

Cyclodextrin nanosponges (CD-NS) are cross-linked polymers made up of cyclodextrins characterized by a nanostructured three-dimensional network. The many hydroxyl groups of CDs permit them to act as multifunctional monomers capable to crosslink with different bi or multifunctional chemicals [1]. The most common batch NSs synthetic pathway, unfortunately, involves the solubilization of the CD in suitable organic polar aprotic liquid, that may affect a potential environmental or biomedical application. The final material has to be accurately cleaned by an extraction procedure with water or volatile solvents, for removing all the solvent inside the batch (and inside the crosslinked structure). At industrial scale, sequentially, the whole process involves huge amounts of solvent to dispose of. Moreover, organic solvents are expensive and, for example, DMSO and DMF are hard to recycle because of the high boiling point. Referring to the Green Chemistry Principles, processes must be designed in order to "minimize the quantity of final waste and to avoid hazardous or toxic solvents". Nanosponges themselves, nevertheless, are obtained from starch derivatives and are biodegradable, so are a remarkably interesting material from this point of view. Since nowadays research is moving towards more sustainable and green approaches, new syntheses of CD-NS are now being developed.

We are here reporting a new green synthesis of nanosponges through a mechanochemical approach. Mechanochemistry involves the application of mechanical forces (compression, shear, or friction) to drive and control chemical reactions, for example using grinding or milling to transfer energy to chemical bonds. Mechanochemistry applied to inorganic chemistry is well established, but in recent years there has been a growing interest in mechanochemistry applied to organic synthesis: esterification and etherification of starch and the possibility of obtaining CD derivatives with a solid state reaction using ball milling, have been reported recently [2]. The green synthetic route here proposed permits to obtain a cross-linked polymer, exhibiting the same characteristics as CD-NS synthesized in batch, without using any solvent. Among the many type of cyclodextrin nanosponges we choose the carbonate NS, synthetized with 1,1-Carbonyldiimidazole as crosslinker, and traditionally synthetized in DMF, toxic and suspected cancerogen solvent.

Furthermore, after the synthesis a significant amount of imidazolyl carbonyl groups still able to react was detected within the NS structure. These reactive groups permitted to obtain a covalent bond between the already synthesized cyclodextrin nanosponges and various organic dyes, with different structures (Methyl Red, Rhodamine B and Fluorescein). The possibility to easily mark with fluorophores CDs and consequently CD-Nanosponges, could open many applications in the pharmacological area, image guided therapies or conjugated drug delivery.

Keywords

Mechanochemistry, Green Synthesis, Cyclodextrin, Nanosponges, Ball-Mill

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Single Cu atom catalyst stabilized in metal oxide for CO_2 hydrogenation

★★

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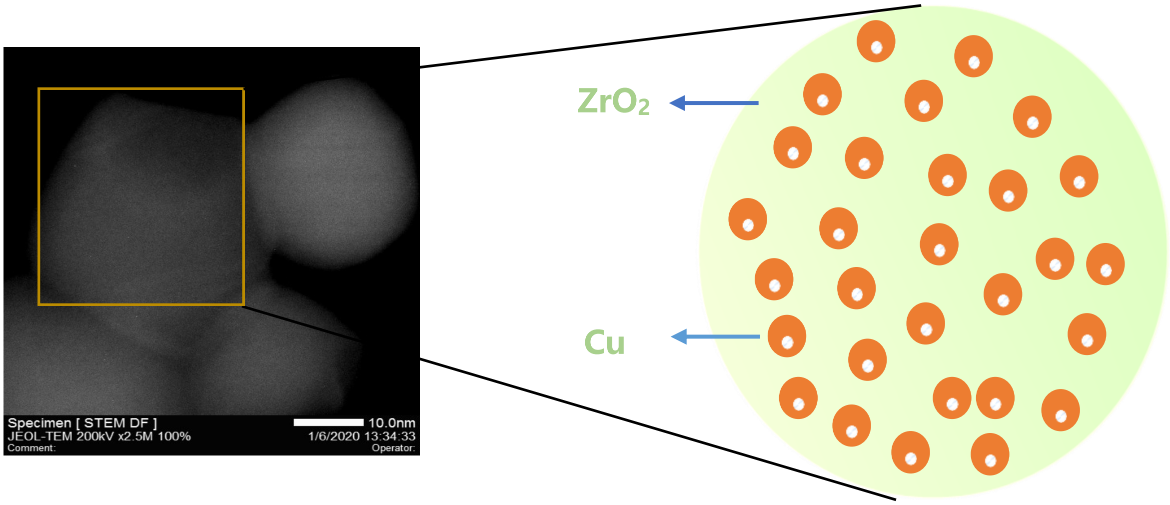
Abstract

Metal single atom catalysts show excellent performance in important catalytic reactions such as oxygen reduction reaction, CO oxidation reaction, conversion of aromatic hydrogen, electrochemical reaction, etc., the construction of highly dispersed metal single atom catalyst system is helpful to recognize the catalysis reaction from the atomic scale, discover new catalysis mechanism, and then promote the development of new industrial catalysts in the fields of energy conversion, environmental catalysis and fine chemicals. The latest research exhibits that the utilize of metal oxides as a support can effectively improve the catalytic performance of metal single atom catalysts. Due to its unique defect sites, it can capture metal atoms. Simultaneously, for easily reduced metal oxides, oxygen vacancies can be formed and unique oxygen vacancies provide anchor sites for stable metal atoms. Herein, we chose zirconia (ZrO_2) as the support and copper nitrate ($Cu(NO_3)_2$) as the metal precursor to prepare Cu single-atom catalyst by the conventional impregnation method. No metal Cu particles or clusters were observed from the following HAADF-STEM, but the Cu content in the Cu/ZrO_2 system was 0.76 wt% by ICP, confirming that Cu atom exists as a uniformly dispersed on the support. Not only is our preparation process simple, but Cu single atoms catalyst have shown excellent catalytic performance in CO_2 hydrogenation.



Keywords: single atom catalyst; metal oxide; CO_2 hydrogenation

Acknowledgements : We are very grateful for the financial support of the National Natural Science Foundation of China (Grant No. 21978043, U1662130).

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Reaction Density Functional Theory towards Green Chemistry

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Abstract

Improving the selectivity and the conversion rate of reaction is an important part of the development of green chemistry. Whereas there are quite a few experiments to improve reaction selectivity and conversion rate by using benign solvents, the mechanism of the solvent effect is not yet clear. The mian difficulty lies in the lack of theoretical models. Very recently, we proposed a multiscale reaction density functional theory (RxDFT) by combining quantum density functional theory for calculating intrinsic reaction energy with classical density functional theory for addressing solvation contribution. RxDFT was further extended to the water-phase reaction[1, 2], the organic-phase reaction[3], and reaction in the confined system[4], and the mechanism of the solvent on several important chemical reactions was successfully described. The development of multiscale RxDFT provides a feasible model for the selection of benign solvents and the study of the mechanism of solvent effect.

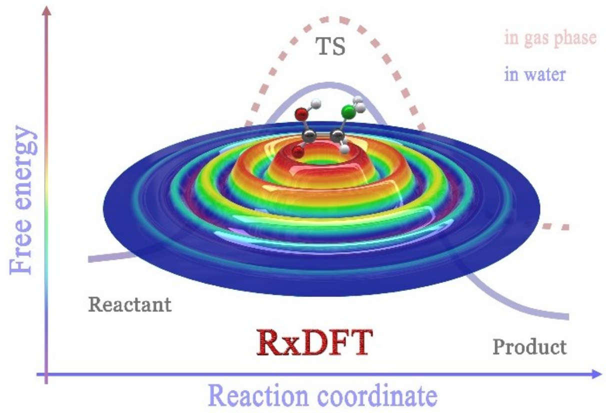

Fig. 1 Development of a reaction density functional theory (RxDFT) by combining quantum density functional theory for calculating intrinsic reaction energy with classical density functional theory for addressing solvation contribution.

Keywords: Reaction density functional theory; Solvent effect; Water; Organic

Acknowledgements

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A more sustainable and highly practicable synthesis of aliphatic isocyanides

★★★★

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Abstract

Synthesis protocols to convert N formamides into isocyanides using three different dehydration reagents (i.e. p toluenesulfonyl chloride (p TsCl), phosphoryl trichloride (POCl3) and the combination of triphenylphosphane (PPh3) and iodine) were investigated and optimized, while considering the principles of green chemistry. Comparison of the yield and the E factors of the different synthesis procedures revealed that, in contrast to the typically applied POCl3 or phosgene derivatives, p TsCl was the reagent of choice for non-sterically demanding aliphatic mono or di N formamides (yields up to 98% and lowest E factor 6.45). Apart from a significantly reduced E-factor, p TsCl is cheap, offers a simplified reaction protocol and work-up, and is less toxic compared to other dehydration reagents. Thus, this procedure offers an easier and greener access to aliphatic isocyanide functionalities,[1] as other routes of synthesis mostly rely on highly toxic compounds like the aforementioned POCl3 or phosgene, triphosgene, TMSCN and AgCN.[2-8]

Figures

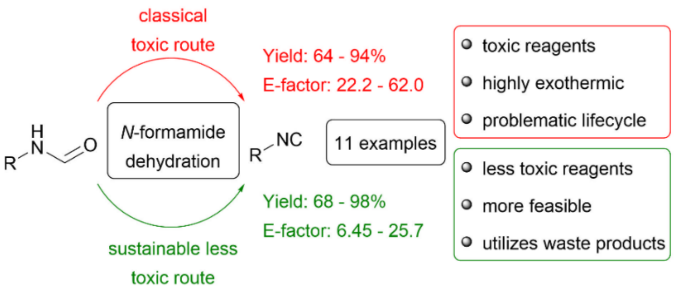

Figure 1: Comparison and optimization of isocyanide syntheses via the classical route utilizing POCl3 and a more sustainable route utilizing p-TsCl.

Keywords: Sustainable Chemistry, Isocyanides, E-Factor

Acknowledgements

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Synthesis of Polyurea via polycondensation of Carbon Dioxide with Diamine Catalyzed by Base Catalyst

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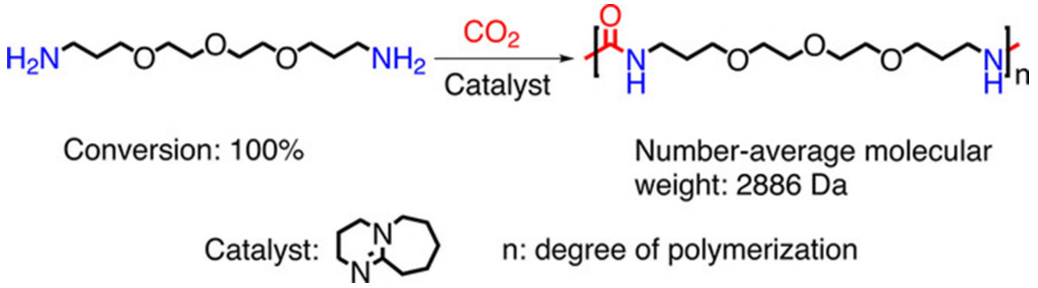
Abstract

Polyureas are a class of polymers that incorporate urea-repeating units in its backbone. One of the noteworthy properties of polyureas is its bidentate nature that allows the formation of multiple hydrogen bonds. These intramolecular hydrogen bonds are responsible for the formation of highly crystalline hard segments, making polyureas mostly insoluble in common solvents. Also, polyureas are extremely resistant to abrasion, high oxidation resistance, good corrosions protection, and are stable at high temperatures, which make them excellent candidates for the preparation of fibers, films, membranes, and coatings. The current typical production of polyurea is based on isocyanate chemistry, where multifunctional isocyanates are reacted with diamine. However, multifunctional isocyanates are toxic and volatile. Therefore, using carbon dioxide (CO_2) as a carbon and oxygen resource to replace isocyanates is an important green process in the fields of chemical synthesis. In this paper, a kind of polyurea was synthesized via the polycondensation of CO_2 with a diamine of 4,7,10-trio a1,13-tridecanediamine (TOTDDA) in the presence of organic or inorganic base catalyst. It was found that 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) was the most active one among the catalysts examined. The influence of CO_2 pressure, temperature, and reaction time was evaluated for the DBU-catalyzed polyurea synthesis. The product formation was confirmed by in situ high-pressure attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) under reaction conditions. A possible reaction mechanism was proposed that in the polymerization DBU can activate both CO_2 and TOTDDA. The polyurea materials synthesized presented high thermal properties as well as high solvent resistance. In addition, the present DBU-catalyzed polycondensation was extended to a wide resource of diamines.



Keywords: carbon dioxide; diamine; polyurea; polymerization; base catalyst

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Enhancing electrochemical CO_2 reduction to C2+ products via Copper-Cerium interface

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Abstract

The accumulation of CO_2 attracts global attention for the resulted Greenhouse effect, leading the diminishment and conversion of CO_2 nonnegligible. Electrochemical reduction of CO_2 is regarded as a promising way to achieve the conversion of CO_2 into the valuable fuels and chemicals, such as CO, ethylene, ethanol, in a mild environment. Compared to C_1 products, C_{2+} products obtain higher value, but confined with the poor selectivity and the low current density.

Here we report one strategy achieve the electrochemical CO_2 reduction to C_{2+} products via the Copper-Cerium oxides catalysts. The Copper-Cerium oxides catalysts were synthesized by the simple coprecipitation way and calcined at a certain temperature. The best Copper-Cerium oxide catalysts performed a high current density above 400 mA cm^{-2} and the Faradaic efficiency of ~ 70% at -1.12 V (vs RHE) in 1 M KOH. According to the characterization of the catalysts and insitu study, we found the formed Copper-Cerium oxides interfaces play an important role in the enhancement of C-C coupling process and thus benefit the C_{2+} products in CO_2 electroreduction.

In conclusion, Copper-Cerium oxides interfaces did favor to the rate-determined C-C coupling step and then enhanced the C_{2+} products in CO_2 electroreduction. This work offers a way to understand the role of interface in CO_2 reduction and may derivates more effective catalysts.

Keywords: CO_2 reduction, electrolysis, metal-oxide interface

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Synergistic catalysis of biological nonmetallic ionic liquid for glycolysis of waste polyethylene terephthalate

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Abstract

The preparation of bis(2-hydroxyethyl terephthalate) (BHET) by glycolysis of waste poly(ethylene terephthalate) (PET) is a green and sustainable technology. Metal residue of traditional catalysts in the products is not conducive to the purification of BHET, thus, it is of great significance to develop nonmetallic catalysts with high efficiency. In this study, several nonmetallic ionic liquids (ILs) based on biological raw materials were synthesized. The synthesized IL catalysts have high catalytic activity in PET glycolysis. The key parameters of the reaction were studied by response surface methodology (RSM) with [Bmim]Pro. Under the optimal reaction conditions (190 ºC, 89 min, ethylene glycol (EG) /PET 5,) predicted by RSM model, the conversion is 100% and the yield is 75.3%. What's more, the error of the model is only 2.84%. The interaction sites among bis(2-hydroxyethyl terephthalate) (BHET), EG and [Bmim]Pro are explored by two dimensional overhauser enhancement spectroscopy (2D NOESY). Then, the mechanism of ester bond fracture catalyzed by [Bmim]Pro was verified by Density Functional Theory (DFT) calculations. Meanwhile, the reaction kinetics was studied which is consistent with shrinking-core model. Finally, the obtained product BHET was highly valuated to prepare polyurethane, and the obtained material was characterized. In conclusion, this work not only proposed a new environmentally friendly catalyst for PET degradation process, but also realized the process from waste PET to high value utilization.

Tables and Figures

Table 1. Catalytic activity of ILs with different anions

ILs	Atomic charges of O on carboxyl of ILs	Conversion of PET(%)	Yield of BHET (%)
[Bmim]Lys	-0.821	99.1	66.4
[Bmim]Pro	-0.853	100.0	75.5
[Bmim]Ala	-0.836	89.2	67.6
[Bmim]His	-0.819	80.3	62.3
[Bmim]Leu	-0.832	86.1	63.4
[Bmim]Arg	-0.815	76.3	26.7

Reaction conditions: temperature 190 ºC; time 120 min; EG/PET/CAT=4:1:0.05

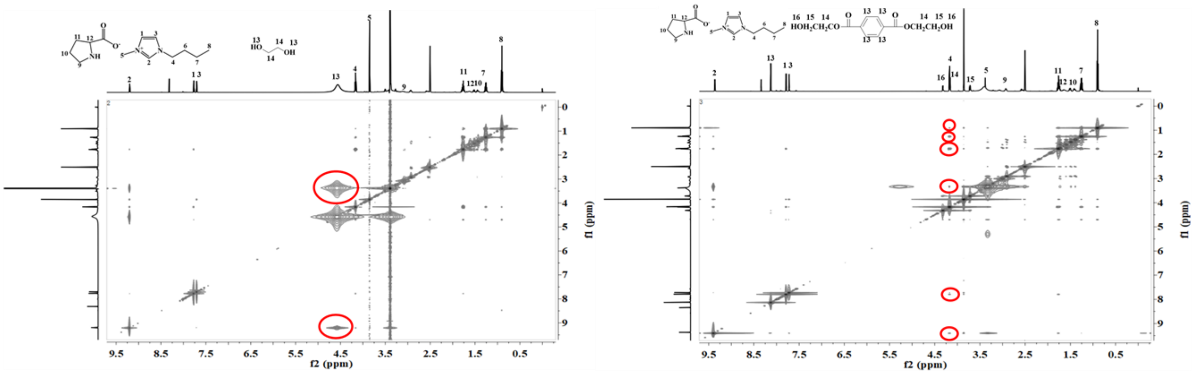

Figure 1. 2D NOESY results about the interactions among BHET, EG and [Bmim]Pro

Keywords

nonmetallic ionic liquids; poly(ethylene terephthalate); degradation; ethylene glycol; Synergistic catalysis

Acknowledgements

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Study on Cloud Point Pressure of [Emim][Tf_2N] in Supercritical Carbon Dioxide Microemulsions Based on Non-ionic Surfactant and Role of Solubilized Water

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Abstract

We studied the solubilization effect of the supercritical carbon dioxide ($scCO_2$) microemulsion based on non-ionic surfactants (Ls-45, Ls-54, Ls-36, Dynol-604, and TMN-6) for 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][Tf_2N]) ionic liquid (IL) as well as the influencing factors by analyzing the cloud point pressure (CPP) curves, which served as a function of dissolved ILs concentration. The [Emim][Tf_2N]/surfactant/$scCO_2$ microemulsion system was characterized by small-angle X-ray scattering (SAXS), which was proved to be a useful method to provide structure and size information of microemulsion. The effect of water on [Emim][Tf_2N]-in-$scCO_2$ (ILs/CO_2) microemulsions was studied. The results showed that the ILs/CO_2 microemulsions could be constructed by five surfactants selected in this paper, and in the Ls-mn system, the Ls-45/[Emim][Tf_2N]/$scCO_2$ system had the lowest CPP. However, the microemulsion constructed by Dynol-604 and TMN-6 surfactants had a poor solubilization effect, and the TMN-6 system was more sensitive to temperature. Besides, small amounts of water could reduce the CPP of the system to a certain extent, making the [Emim][Tf_2N]/surfactant/$scCO_2$ microemulsion system more stable, which had a positive effect on the solubilization of [Emim][Tf_2N], especially the Ls-36 system. Moreover, the size of microemulsion droplets in [Emim][Tf_2N]/surfactant/$scCO_2$ systems was obtained by using the method of SAXS experiment, which also confirmed the solubilization of [Emim][Tf_2N] in $scCO_2$ microemulsion system. The structure of ILs/CO_2 microemulsions constructed with a non-ionic surfactant was speculated. This study can provide a reference for the construction of ILs/CO_2 microemulsions, which was helpful in understanding the microstructure and solubilities of ionic liquids in $scCO_2$ microemulsions.

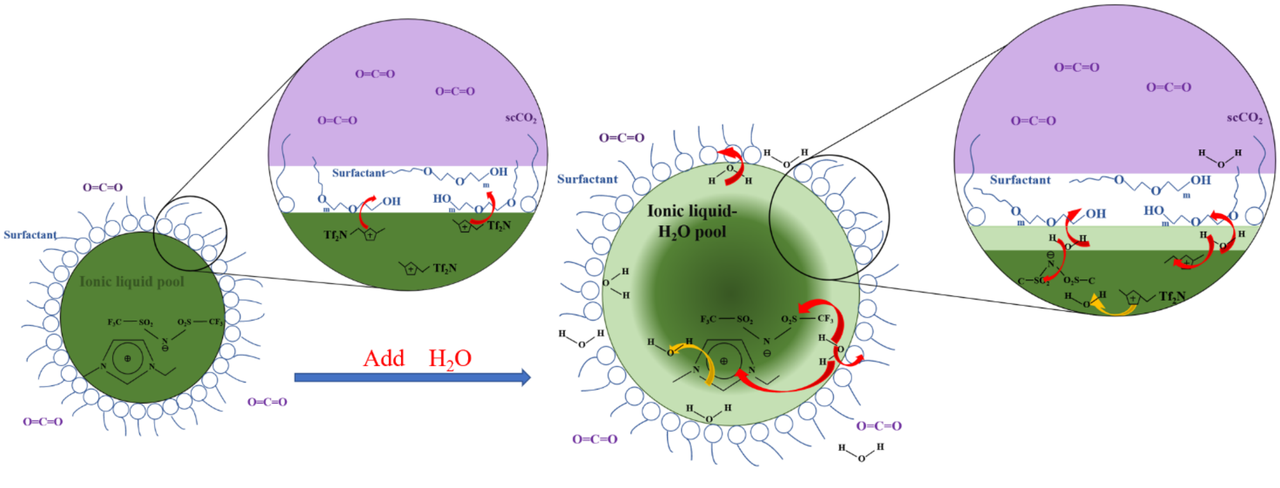

Figure. Possible structure of the [Emim][Tf_2N] (+H_2O)/CO_2 microemulsion.

Keywords

Supercritical CO_2 microemulsion; [Emim][Tf_2N]; Cloud point pressure

Acknowledgements

U1662130; 21506027; DUT17JC34

Oxidation of Xiaolongtan lignite to oxygen-containing chemicals over $H_5PV_2Mo_{10}O_{40}$-H_2SO_4 by introducing methanol to suppress the formation of CO_2

★★

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Abstract

The production of carboxylic acid from lignite via catalytic oxidation with O_2 is an effective method. However, because of the peroxidation, a significant amount of CO_2 is generated, reducing the utilization of carbon in lignite. To suppress CO_2 production, we introduced methanol into the $H_5PV_2Mo_{10}O_{40}$-H_2SO_4 aqueous solution to produce oxygen-containing chemicals from lignite. The oxygen-containing chemicals mainly include carboxylic acids, methyl formate, and methylal. The yeild of CO_2 is 32% at a methanol content of 40 vol%, while in $H_5PV_2Mo_{10}O_{40}$-H_2SO_4 aqueous solution it is 56%. The previous work of our research group also found that methylal is produced via the acetalization between methanol and aldehyde, and the reaction changes the pathway of aldehyde conversion into carboxyl. Meanwhile, ester is generated via esterification between methanol and carboxyl group, protected against decarboxylation to CO_2. These acetalization and esterification suppress CO_2 generation. Introducing methanol into $H_5PV_2Mo_{10}O_{40}$-H_2SO_4 aqueous solution improves the utilization of carbon in lignite significantly.

Keywords: Lignite oxidation, CO_2, Suppression, Methanol, Acetalization, Esterification

3. ENERGY SAVING

High pressure switchable water: A path towards greener biomass conversion

★★★

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Abstract

Separation of organic products from water is so environmentally and economically costly that biomass-derived products struggle to compete against petrochemicals. The separation of organic solutes from water is a focus point considering that such separations are core in the biomass conversion sector, which relies on reactions taking place in water [1]. Currently, industries rely on thermal processes such as distillation and evaporation [2]. As a result, improvements to the current chemical separations could potentially lead to a reduction in energy consumption. We proposed a new approach for chemical separations utilizing CO_2 switchable solutions as a strategy to mitigate the energy impact of separations. This strategy relies on high pressure switchable water (HPSW). HPSW is a process that combines CO_2 expansion of liquids (CXL) and switchable water (SW). CXL utilizes high-pressures of CO_2 to promote changes to the polarity of organic solutes, decreasing their solubility in water [3]. SW utilizes tertiary amines that upon contact with CO_2 form bicarbonate salts that change the ionic strength of the aqueous solution, which creates a salting-out effect facilitating the removal of organic solutes [4]. Although both processes were shown to trigger the separation of some organics from water, they are not efficient for the removal of hydrophilic solutes and the phases obtained after separation are not sufficiently pure. We hypothesize that CXL and SW, if performed simultaneously, would act synergistically and as a result, promote more efficient and cleaner separations. If HPSW can promote better separations, then considerable savings in the energy utilized for separations could be achieved. We carried out experiments with acetone, a solvent with high miscibility in water, that previously could not be separated with SW alone and required 26 bar of CO_2 to be removed via CXL. We screened a range of SW additives for their efficacy in separating acetone:water solutions. All the additives tested were able to separate 50:50 acetone:water solutions at lower pressures than CXL. The best amine tested was able to decrease the separation pressure to 2 bar of CO_2, and it was better than CXL in the entire range of acetone:water compositions. Therefore, we envision HPSW being very effective with other valuable chemicals that might be obtained from biomass, such as ethanol and diols. By doing so, the current issues related to the high energy consumptions in the biomass sector, which can be a barrier for their adoption over petrochemicals, might be overcome with the utilization of HPSW for enhanced separations.

Keywords

water chemistry, amines, carbon dioxide

Acknowledgements

Natural Sciences and Engineering Research Council (NSERC) and Department of Chemistry Queen's University.

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Developing Truly Green Solar Cells

★★★

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Abstract

With the demand for energy growing, so is the need to find a renewable energy source, in which solar energy has become a front runner. It has been predicted the growth in solar energy will reach 4500GW by 2050. [1] This level of growth would add enormous stress to supply chains for raw materials, whilst also increasing dramatically the amount of waste produced. It is predicted by 2050 there will be between 68-75 million tons of photovoltaic waste. [1]

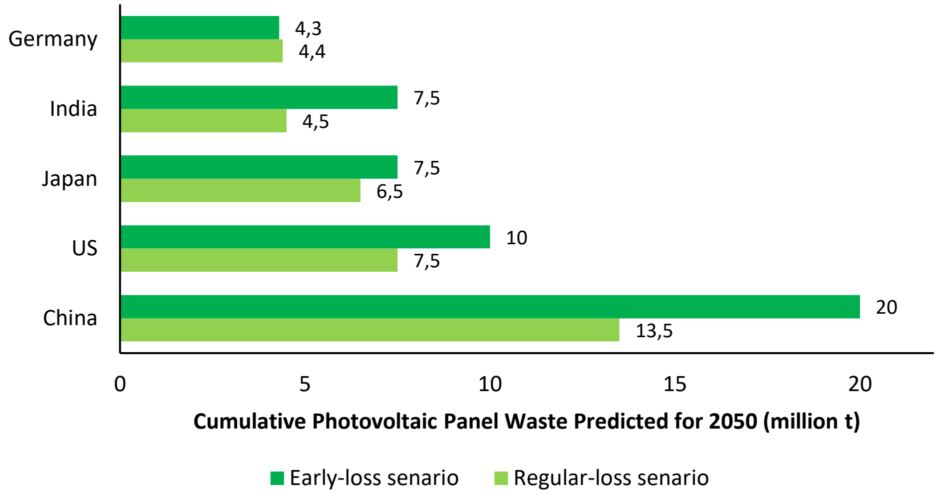

Figure 4: Graph showing the predicted waste generated by photovoltaics (PV) by 2050 from the five countries installing the highest quantities. Figure has been redrawn.[1]

To address these issues, the idea of a truly green solar cell was developed. This concept aims to reduce demand on resources by minimising the use of raw materials and consider the lifetime analysis of the devices. Some potential methods of addressing these aims include, recycling to create a circular economy for photovoltaics, and utilising waste produced by other industries for solar applications. The idea of the circular economy for solar cells will ensure the materials present at end of life can be extracted and recycled. It is important to extract the materials present in photovoltaics, as some materials used are considered rare earth metals with limited natural resources. One example of these is indium, in 2011 it was predicted the supply of indium could fail to meet demand by 2020. [2] By taking this circular economy approach, it could help encourage a sustainable method of producing solar cells. Another way of creating a truly green solar cell, is to source materials from other waste streams. The waste streams which are of interest are mining wastewater, surrounding soil and used batteries. These sources can offer a wide range of different materials. If it is possible to successfully extract the materials present, it gives the potential for a sustainable and environmentally conscious method of sourcing materials for photovoltaic production.

Keywords: Solar Cells, Renewable Energy, Circular Economy

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Synthesis and Characterization of TiO_2 Nanoparticles Prepared Using Natural Extract of Adansonia Digitata.

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Abstract

In this work, we report the synthesis and characterization of titanium dioxide nanoparticles (TiO_2 NPs) using natural extract adansonia digitata leaves. The Structural and optical properties of the prepared NPs are characterized using several spectroscopic and microscopic methods including X-ray diffraction, Raman, UV-Vis, ATR-FTIR, Photoluminescence, and HRTEM.

Synthesized samples annealed at various temperature of 700°C, 800°C, 900°C reveal Bragg peaks which were matched to tétragonale structure of TiO_2 while ATR-FTIR analysis show absorption bands around 498 cm^{-1} characteristics of TiO_2 NPs. Photoluminescence spectroscopy analysis shows a higher emissions peaks around 410 nm, 419 nm, and 427 nm, meanwhile diffuse reflectance measurement recorded reflectance of 57%, 82 %, 90 % and 97% for samples no-annealing and annealed respectively at 100°C, 700°C, 800 ^{0}C, and 900 ^{0} C. One distinguish seven active Raman modes: five Eg modes centered approximately around 163 cm^{-1}, 239 cm^{-1}, 360 cm^{-1}, 483 cm^{-1}, and 606 cm^{-1}. Another important observation of our results from the TEM is the presence of mostly small NPs; however, relatively larger NPs were also present. This indicates a bimodal size distribution for the synthesized NPs.

Keywords : Biosynthesis, Titanium Dioxide Nanoparticles, Adansonia Digitata

Tailoring high-quality fuels with renewable biomass

★

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Abstract

The rising global concerns on energy and environment have intensified the interest in the utilization of clean and renewable energies. Biomass is the only renewable source of organic carbon in nature, and its conversion to a variety of value-added chemicals and liquid fuels has attracted increasing attention. Generally, the production of long-chain alkanes from biomass or its-derived compounds goes C-C coupling and hydrodeoxygenation [1]. Straight-chain alkanes have poor property and must be blended with branched alkanes to decrease the freezing point or cycloalkanes to increase the density. Therefore, tailoring high-quality fuels with biomass or its-derived compounds is of significant importance.

We developed a novel process for converting furfural into liquid transportation fuels through three consecutive catalytic steps that involve aldol condensation, Michael addition, and hydrodeoxygenation (Figure 1a) [2]. The obtained alkanes possess excellent branched chain structure, accordingly contributing to low freezing point and can be directly blended with conventional transportation fuels or as components of lubricants. The Michael addition product, amulti-carbonyl compound containing active a-H atoms, can be used to perform intramolecular aldol condensation to produce cyclic oxygenates. This tandem reaction of Michael addition and intramolecular aldol condensation is known as Robinson annulation. We achieved the first example to use Robinson annulation to construct biofuels (Figure 1b) [3]. Low-freezing-point and high-density highly branched alkylcyclohexanes were produced through two steps, namely, a one-pot cyclization process including the aldol condensation of furfural with 2,4-pentanedione and the subsequent Robinson annulation of the aldol adducts with 2,4-pentanedione over $CoCl_2 \cdot 6H_2O$ catalyst, then following with the $Pd/NbOPO_4$-catalyzed hydrodeoxygenation.

The efficient utilization of renewable glucose has enormous potential to reduce the excessive dependence on fossil resources, but remains challenging owing to the inevitable formation of undesirable humins and multistep processes. Reported here is a new 2,4-pentanedione/H 2 O–NaCl biphasic system for the direct one-step conversion of glucose to high-quality fuel precursors with a high utilization efficiency of glucose (90%) (Figure 1c) [4]. The formation of humins is markedly restrained with an entirely new pathway, i.e. glucose directly reacts with 2,4-pentanedione to afford fuel precursors via several chemical transformations, which is totally different from the traditional glucose-to-fructose-to-HMF way. Control experiments and DFT calculations confirm that this new pathway is thermodynamically favorable compared with the traditional way. This simple system is also capable of converting starch to fuel precursors, paving a new way for the efficient valorization of glucose-based natural sugars.

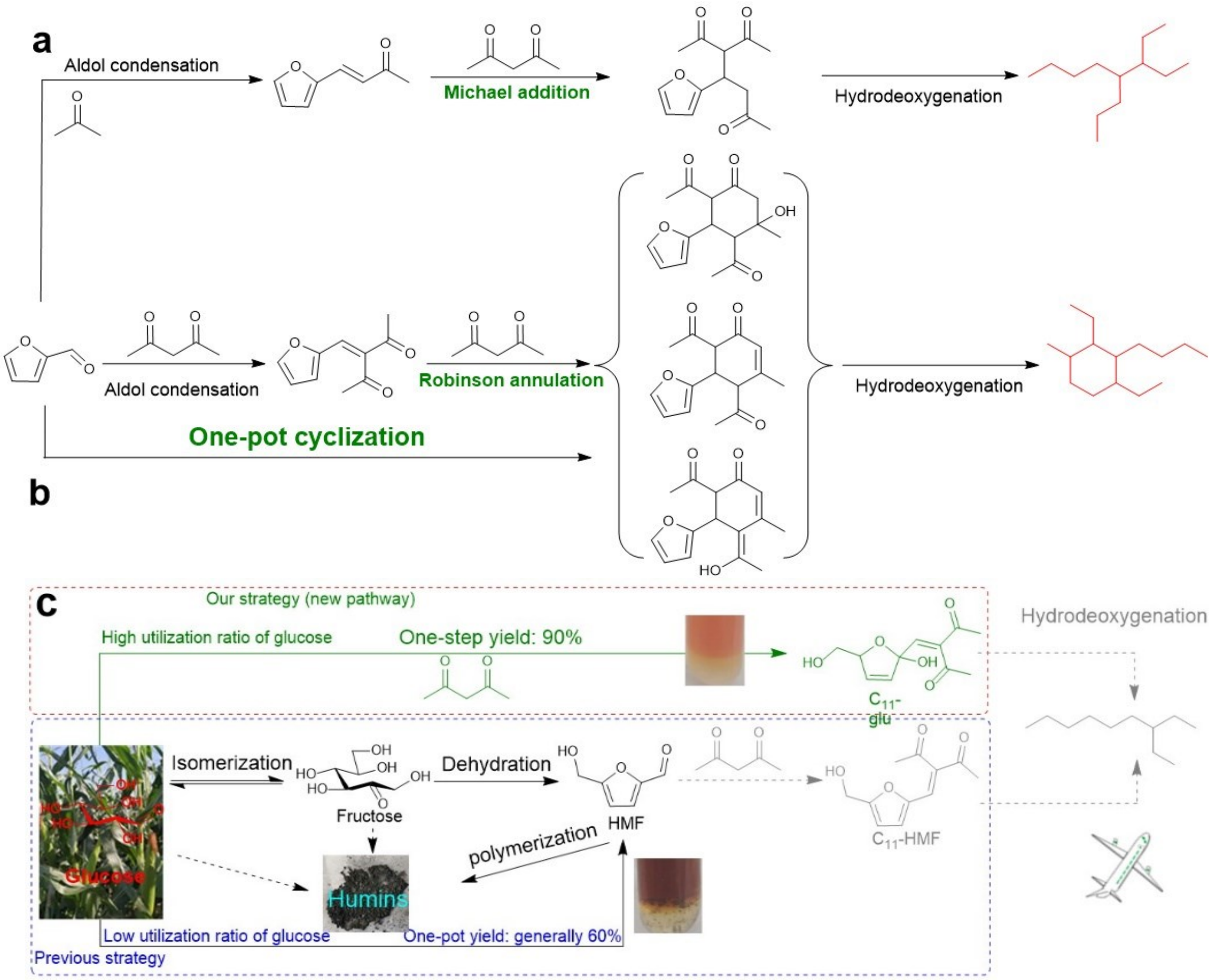

Figure 1. Tailoring high-quality fuels with renewable biomass

Keywords

Biomass, jet fuel, glucose, Michael addition, Robinson annulation

Acknowledgements

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Structural evolution characteristics of Huolinhe lignite during heat treatment: Based on coal oxidation

★★

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Abstract

According to statistics, coal is likely to remain the main energy source in the foreseeable future. Heat treatment is the commonness and key of coal transformation. Coal gasification, liquefaction and other processes need to go through heat treatment. The research on the structural change of coal in the pyrolysis process can provide a basis for the comprehensive utilization of coal, which is of great significance for the coal transformation. Moreover, understanding the structural changes of coal in the pyrolysis process is helpful to comprehend the process of coalification.

From the perspective of oxidation, the yield distribution of benzene carboxylic acid in the products can reflect the structure of different char, which is a new idea to study the structural change of coal during the pyrolysis. In this work, alkali-oxygen oxidation, combined with ultimate analysis, ^{13}C NMR, FTIR of raw coal and its chars was used to reflect the structural changes of coal during pyrolysis. With increasing temperature, the aliphatic side chains of coal are constantly cracked, the oxygen-containing functional groups are reduced, and the degree of aromatization of coal may be increased.

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Electrochemistry

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Abstract

Lignin valorization is challenging because of the complexity and recalcitrance of the lignin structure. In addition, conventional methods such as pyrolysis and acid/base hydrolysis often required harsh conditions like high temperature and/or high pressure, expensive and/or toxic catalysts [1]. The current research aims to address the aforementioned challenges by utilizing electrochemistry as a “greener” technology for depolymerization of a recently discovered, linear and homogeneous lignin, named C-lignin [1]. C-lignin was discovered in vanilla seed coats and is found in different nut shells. C-lignin is composed of caffeyl alcohol units linked through benzodioxane linkages [2].Hence C-lignin depolymerization by benzodioxane cleavage could provide a renewable source of catechol.[2] Electro-organic synthesis is a promising technique for lignin valorization because it can be operated at low temperature and pressure using electric currents as an inexpensive safe reagent. However, low yield, poor selectivity, and lack of mechanistic understanding are challenges that remain to be addressed. It is thus necessary to develop robust electrocatalysts that are highly active and selective towards C-lignin electrocatalytic cleavage. The study aims to elucidate the mechanism of electrocatalytic C-lignin depolymerization via utilizing model compounds with the ultimate goal of designing effective electrocatalysts for valorization of C-lignin.

Keywords

Lignin depolymerization, C-lignin, Electrochemistry, Electrocatalysts

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Bio-inspired of Fe doped $BiVO_4$ Nanoparticles via *Hyphaene thebaica* natural extract and their photocatalytic MB degradation properties.

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Abstract:
This contribution reports for the 1st time on the bio-synthesis of Fe doped $BiVO_4$ nanorods using extracts of Hyphaene thebaica as an effective chelating and capping agent. Their surface & interface properties of such Fe: $BiVO_4$ nanocrystals were investigated via several complementary techniques including X-Ray diffraction analysis (XRD), Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (TEM), & Selected Area Electron Diffraction (SAED),as well as Electron Dispersion X-ray Spectroscopy (EDS), UV-VIS diffuse reflectance spectroscopy (DRS), Fluorescence, and Raman Spectroscopy. The study confirmed the single phase crystalline BiVO4 phase with Fe as an interstitial dopant. The major effect of the Fe doping was correlated to the optical bandgap tunability. Th annealed Fe:$BiVO_4$ 1-D nano-crystals were found to exhibit a significanton photocatalytic degradation of methylene blue (MB) in the Visible spectral range

Eco-friendly hybrid capacitor based on Ni/Al Layered Double Hydroxide and reduced Graphene Oxide composites

★★★

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Abstract

The global demand on energy grows and renewable resources are the only possible tools to rely on for the future. The most relevant problem is that they tend to be intermittent and unpredictable. As a result, there will be an increasing need to store this energy. Supercapacitors have drawn a lot of attention in this field. In this scenario, layered double hydroxides (LDHs), also known as anionic clays, containing redox active transition metals are attractive compounds. [1] However, many LDH applications are still largely restricted due to their low electrical conductivity. Of course, this reduces the performances of electrochemical devices: in particular, supercapacitors need high currents flowing during fast charge−discharge cycles. These weak points can be overcome by combining LDHs with carbon nanomaterials, such as graphene. In the present work, we propose a one-step electrosynthetic protocol that produces nanostructured films of composites based on Ni/Al-LDH and reduced graphene oxide (GO).[2] This procedure contemporaneously allows for the LDH synthesis, the reduction of GO and its intercalation inside the layered structure as ERGO. Up to date, the only interlayer anions introduced in LDHs coming from electrochemical syntheses are small molecules. This greatly constrains the LDHs applicability: in particular, our work could pave the way for further studies in the field of electrochemically induced intercalation chemistry. The films obtained have been thoroughly characterized by many techniques in order to verify the structure and morphology of the composites and to propose a theorization of the synthetic and growth mechanisms. Ultimately, we were able to employ these composites in the field of energy storage: the proposed hybrid super capacitor had a starting discharge specific capacity of 880 F g^{-1} which decreased and stabilized at 820 F g^{-1} after 300 cycles. The potential applicability of the device was also demonstrated by powering a red light-emitting diode. This work embraces the necessity of the development of systems with low environmental impact: in fact, we have proposed a binder-free device, safe, composed of hearth abundant element and able to work in aqueous electrolyte system with high performances. [3]

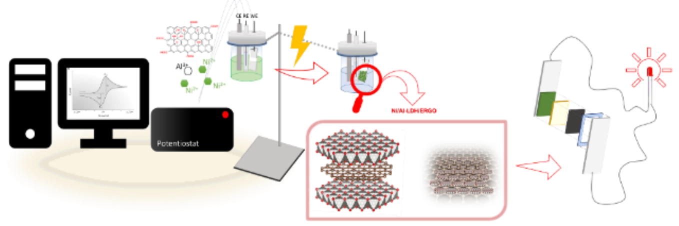

Figure 5: Sketch of the proposed work

Keywords: Layered Double Hydroxide, Electrochemical Synthesis, Hybrid Supercapacitor

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Selective Oxidation of Methane

★★★

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Abstract

Methane is a valuable resource. Frequently, due to its transportation and compression being uneconomical, it is combusted at site of the refinery without any useful work being extracted. This, not only adds to the greenhouse gases in the environment, but also is a wastage of valuable fuel which can be used to produce energy or used as a raw material to make a wide range of industrial chemicals[1]. The project discussed here, aims to find a suitable catalyst to provide us with the most economical way for the selective oxidation of methane (gas) to methanol (liquid). The phase change from gas to liquid will not only make the transportation easier, thereby preventing its useless combustion, but also serve as a cheap source of a valuable industrial raw material[2]. The project explores various catalytic pathways by which this can be done, methods by which the performance can be characterized as well as the room for improvement in future related research projects.

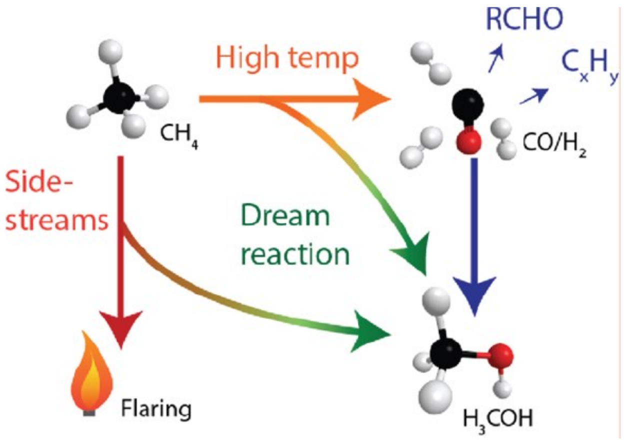

Figure 6 Reaction pathways for selective oxidation of methane[3]

Keywords
Methane, Catalytic engineering, selective oxidation

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Perovskite Catalyst for Heterogeneous Aerobic C-H Oxidation Reactions

★★★

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Abstract

C–H activation has become a powerful tool in molecular synthesis in recent years.[1] Although there are extensive developments, catalytic oxidation of C-H bonds is usually accomplished by using precious noble metals and thus the need for cost effective catalysts emerged. Lately, the search for alternative ways that use less expensive and toxic first row transition metals such as manganese to replace these expensive metal catalysts still endures.[2] Also, typical oxidation processes use excess amounts of toxic organic/inorganic reagents, hence developing a new method that employs molecular oxygen as the oxidant will have the potential to be beneficial in environmental and economical contexts.[3] As an oxidant, molecular oxygen is green, cheap, clean and readily available in nature. However, it is relatively unreactive toward the strong C–H bonds unless it is activated by highly efficient catalysts.

In this work, we have developed a pretreatment system to increase the activity of $LaMnO_3$ perovskites in order to achieve catalytic aerobic C-H oxidation reactions of numerous compounds in mild conditions as a general requirement of green chemistry. The fact that this catalyst is heterogeneous provides easy separation. Besides, the low cost and high stability of the $LaMnO_3$ perovskite make it a valuable candidate for the catalytic oxidation of unactivated C-H bonds.

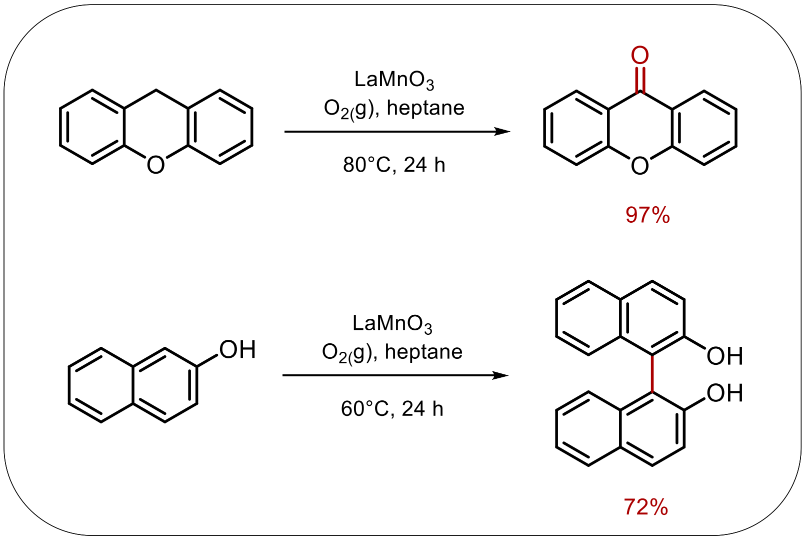

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Figure 7: Synthesis of the Oxidation Products

Keywords: C-H functionalization, aerobic oxidation, heterogeneous catalysis, perovskite

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Effect of Ni NP morphology on catalyst performance in non-thermal plasma-assisted dry reforming of methane

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Abstract

Global energy consumption currently stands at 14 BToe, 83% of which is supplied by fossil fuel combustion [1]. With carbon emission targets set by the IPCC to reach net zero by 2050 the need for reliable, renewable energy sources is urgent [2]. The transient nature of renewables such as wind and solar electricity mean supply is not constant. During times of excess, electricity can be put towards powering endothermic chemical processes to store the energy. Dry reforming of methane (DRM) is one possible process, converting ubiquitous CO_2 and CH_4 into CO and H_2 (syngas), which can then be sold as the precursor to liquid fuels or back reacted to supply energy when renewable energy generation is low. The DRM process has some major limitations to its viability as an industrial full-scale process, i.e. the need for (i) temperatures above 1000 ºC, (ii) noble metal catalysts to achieve high conversions, (iii) equilibrium limitations, and (iv) severe carbon deposition, deactivating the catalysts. Transition metals such as Ni have shown good activity in this reaction but still suffer from carbon deposition [3]. The characteristics of non-thermal plasma make it an idea candidate for use in the generation of solar fuels. The reaction is instantaneous, proceeds at room temperature and atmospheric pressure. Excess renewable electricity can be used to generate a plasma, which in turn can be used, in the presence of a catalyst, to promote the DRM reaction. The use of plasma-catalyst hybrid systems has also shown synergistic effects with high conversion rates in the DRM reaction [4].

In this work a range of Al_2O_3 supported Ni catalysts with varied Ni nanoparticle morphology were hydrothermally synthesised. Characterisation methods include XRD, SEM/EDX and FTIR. The catalytic activity of the materials was tested in a spark-discharge plasma reactor for the DRM reaction and monitored via GC and MS analysis. It was found that Ni NP deposited catalysts showed up to 31% higher conversion of CH_4 and 24% higher CO_2 conversion than conventional wet-impregnated materials (fig 1). All materials tested showed a selectivity towards hydrogen production over CO, suggesting CH_4 decomposition as well as dry reforming.

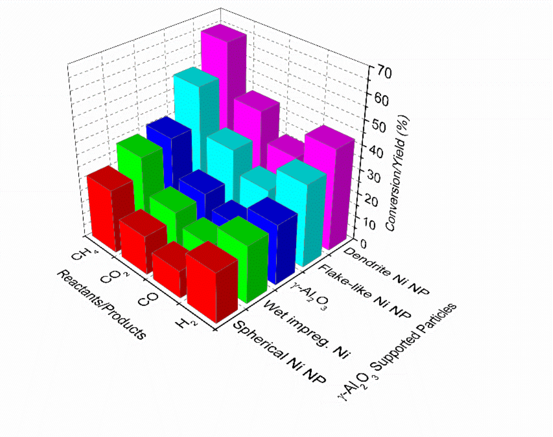

Fig. 1 Bar chart showing percentage conversion and yields of CH_4 and CO_2 into CO and H_2 in the plasma-assisted DRM reaction

Keywords

Solar fuels, renewable energy, catalysis, non-thermal plasma

Acknowledgements

Thank you to the Irish Research Council for funding this work

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Dual-Function Textile Supercapacitor: A New Green & Sustainable Energy Storage Device

★★★

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Abstract

The rapid growth of the global population and economy triggered an increasing demand for energy. The Era of the Internet of Things is marked by an exponential use of portable energy-consuming products [1]. Due to that, more than 3 billion of batteries containing hazardous materials are disposed in landfills, every year (in USA), posing a major threat to health and to the environment. Supercapacitors (SCs) have attracted great attention as an eco-friendly alternative to batteries, presenting significantly higher cycle life ($>10^5$ *vs.* ~1500 charge-discharge cycles) and faster charging [2]. Carbon nanomaterials (CN) have been reported as remarkable electrode materials for the fabrication of energy storage devices with high power density and cycling stability [2]. Nowadays, the fabrication of SCs in textiles or fibers has been boosting the development of wearable energy storage systems in order to power electronic devices integrated on clothes while, at same time, maintaining flexibility, lightness and comfort features. Recently, several efforts have been made to fabricate multifunctional wearable devices that store energy while at the same time changing their optical properties upon light irradiation, namely to produce safety wearing for nighttime users [3].

In this work, a dual-function fluorescent textile SC with the ability to store energy while simultaneously exhibiting an optical response to the action of UV light, was produced through an eco-sustainable and scalable process. To achieve that goal, textile substrates were coated with CN and a fluorescent pigment (FP) and used as electrodes to produce the smart textile SC (SC_CN_FP). For comparison, a non-fluorescent SC was also produced (SC_CN).

Characterization techniques, including XRD and SEM-EDS, confirmed the successful preparation of the textile electrodes. The electrochemical performance of the SC_CN_FP and SC_CN textile SCs was assessed. The SC_CN_FP presented 1.7× higher power density than SC_CN (574.2 *vs.* 342.9 W kg^{-1}), as well as 1.5× higher energy density (1.63 *vs.* 1.10 W h kg^{-1}), confirming its potentialities as energy storage system. These achievements were assigned to the occurrence of both non-faradaic (electrostatic) and faradaic (redox reactions) charge storage mechanisms. Finally, the SC_CN_FP exhibited excellent cycling stability (~100%) after 10000 cycles and its exposure to UV light ($\lambda = 365$ and 254 nm) confirmed its fluorescent properties, reflected in a yellow/orange color.

Keywords: carbon nanomaterial; multifunctional smart textile; energy storage.

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Flexible Pressure Sensor Based on Silver/Graphene Nanocomposites Was Prepared By One Step

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Abstract

Flexible pressure sensors are the core component of flexible wearable device, which have great application potential in many fields. Graphene is an excellent sensitive material for flexible pressure sensors. Graphene is an excellent sensitive material for flexible pressure sensors. However, due to the defects of grain boundary or stacking caused by graphene fragments, the flexible pressure sensors using pure graphene have problems such as low sensitivity, poor stability and so on. Silver nanomaterials and graphene can be used to construct composite materials, which can effectively span the defect or lap adjacent laminates.

Keywords: Graphene, Silver Nanoparticle, Sensor, One Step.

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4. FOOD SAFETY

Comparative Study On The Environmental / Oral Health Effect Of Neem Twigs And Synthetic Toothbrush

Chiemena AMADI, Linda OKIKE, Judith ANOSIKE, Dr C.O ALISA

Abstract

1.1 Background

A study was conducted to survey the effect of the use of neem twigs on the oral health and the environment as opposed the conventional toothbrushes and mouthwash

It has been stated that more than 30% of the entire plant species at one time or the other are used for medicinal purposes necessary due to the amount and type of secondary metabolite they contain [1]. *Neem* tree, the ”tree of a thousand trees” have been used for medical, cosmetic, agricultural and other purposes due to its antifungal, antiviral, pest-control, sedative and many more effects. *Neem* extracts can also be found in *Ayurvedic* and other toothpastes [2].

Some African chewing sticks are also reported to contain fluoride ions, silicon, tannic acid, sodium bicarbonate and natural plaques inhibiting substances that can reduce bacterial colonization and plaque formation [3].

Dried chewing sticks of *Neem* showed maximum antibacterial activity against S. *mutans* compared to other dental caries-causing organisms, *S. salivarius, S. mitis, and S. sanguis* [4].

Aqueous extract of neem twig and the gallotanin-enriched extract from *Melaphis chinensis* inhibited insoluble glucan synthesis and results in bacterial aggregation. It reduces the inability of *streptococci* to colonize tooth surfaces [5].

1.2 Introduction

The ancient Nigeria civilization were reported to use *plant* twigs and sticks for brushing their teeth using the edge of the twig/stick, chewed to soften to form bristles to clean teeth .

In Sokoto, Neem trees serves as a source of covering or shed from the sun, due to the temperate condition of the environment. Plants hardly thrive naturally on its soil but, neem trees grow well in the region, this has caused the inhabitants of Sokoto to derive pleasure in neem tree planting as a source of shelter from the sun and as a method of observing a green environment. The twigs of this tree are easily accessible for the cleaning of the teeth and treating of various dental infections.

According to the producers' information most of the common toothbrushes are made of thermoplastic, e.g. polypropylene, SAN (Styrene-Acrylic Nitrile- copolymer) or other styrene copolymers. The bristles are made of polyamide [6].

1.3 Materials and methods

1.3.1 The study area

Geographically, Sokoto is located in the extreme Northwest part of Nigeria, The state covers a total of 25 973km^2 (10 028sq mi) area. Sokoto’s coordinates are latitude of 13^{0}15^1 N and the longitude of 05^{0}15^1 E, with a total population of 3,702,676 people (according to the last census carried out in 2016).

The study was carried out from 2019-2020, with visits to rural and urban area in different communities in 9 districts; Sokoto south, Sokoto north, Wamakko, Dange shuni, Shagari, Illela, Bodinga, Achida, and Wornu –with their languages mainly Hausa and Fulani.

The information gathered were from age group 8-18, 30-45, and above 45 years old. At least, 7 to 12 person of each age group including old women from the communities we visited, data was recorded on the use of neem twigs.

1.4 Conclusion

For better storage and preservation, neem twigs are best wrapped in paper bags and stored in a refrigerator to avoid molds growing on them [7].

Neem twigs are cost effective; this a basic advantage compared to toothbrushes (which requires a toothpaste before it can be used) and synthetic mouth wash. Neem twigs can be used for longer duration.

Keywords: Neem twigs, oral and dental hygiene, tooth brush, mouthwash,

Acknowledgement

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Comparison of Extraction Technique on Hypoglycaemic Activity of Ethanolic Extract of *Acacia arabica* Plant

★★★

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Abstract

Diabetes is a pandemic chronic condition associated with abnormalities in carbohydrate, protein & fat metabolism and can be responsible for severe disorder. Scavenging free radicals is a way to reduce the oxidative stress. Natural products especially from plants sources have the ability to reduce oxidative stress by acting as antioxidant[1].Traditional plant *Acacia arabica* is a rich source of phytochemicals, have great medicinal value and used in folk medicines[2]. Aim of the present study is to confirm the hypoglycaemic effect of *Acacia arabica* plant and to compare the efficacy of different extract in-vitro against α-amylase one of the key enzyme responsible for digestion of carbohydrate.

In this study leaf, bark and flower of *Acacia arabica* were extracted by traditional Soxhlet method and modern microwave assisted extraction method using ethanol as solvent. All the extracts were screened for the presence of alkaloids, saponins, phenols, tannins, flavonoids, sterols, carbohydrates. These extracts were estimated for the presence of Total Phenolic Content (TPC), Total Flavonoid Content (TFC) and Total Tannin Content (TTC). In-vitro alpha amylase inhibition assay was performed using the 3,5-dinitrosalicylic acid solution and used acarbose as standard. Absorbance was measured at 540 nm by UV-Visible spectrophotometer. The percentage inhibition of the α- amylase by plant extract and acarbose were determined.

All the extracts of *Acacia arabica* plant showed considerable antidiabetic potential when compared with acarbose. The microwave assisted ethanolic bark extract of *Acacia arabica* exhibited remarkable α- amylase inhibitory activity . The presence of phytochemicals like phenols, flavonoids , tannins and others like alkaloid, saponins may have contributed greatly to the inhibitory activity of the plant extract[3,4]. Ethanolic bark extract of *Acacia arabica* can be used as alternative medicine for the management of diabetes.

Key words: Acacia arabica, extraction, phyto-chemicals, antidiabetic potential,

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Characterization and Evaluation of *In vitro* α-glucosidase Inhibitory Property of Cacao (*theobroma cacao*) Pod Husks Extract: A Potential Source of Herbal Supplement

★

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Abstract

Municipal waste has generated 2.01 billion tons annually of solid waste of which 44% derived from green and food products. Untreated food waste contributes about 1.6 billion tons of carbon dioxide (CO_2) and methane (CH_4) greenhouse gases that significantly influenced earth climate [1]. However, exploring the use of food wastes as alternative medicine is feasible as it contains bioactive compounds such as antioxidants, pectin, minerals, dietary fibre, and methylxanthines [2-3]. On these facts, this study utilized locally available cacao pod husk (by-product of chocolate production) as probable alternative source of herbal medicine. The plant material was collected at Malagos Calinan, Davao City Philippines. It underwent experimental analyses for heavy metals (Cd and Pb) and mutagenicity assay to establish that the cacao pod husk is non-toxic. The phytochemicals constituents, mineral content (Magnesium, Mg), and pharmacological activities as antioxidant and α-glucosidase inhibitor were also determined. Results of the test revealed that the levels of toxic heavy metals (Cd & Pb) conformed to the maximum allowable limit of Philippines Food and Drug Administration (FDA) for herbal preparation [4]. The plant is non-mutagenic as there was no substantial increased in the formation of revertant colonies at concentrations of 0.04-5.0 mg extract per ml solvent [6-7]. Meanwhile, the cacao pod husks (CPHs) contained phenolics, flavonoids and Magnesium at a concentration of 20.64ppm, 10.86ppm, and 0.083% (w/w), respectively. This suggests that CPHs can be an excellent source of dietary quercetin and Magnesium [8-10]. The tests for antioxidant property and α-glucosidase inhibitor activity were done using three solvents (ethanol, hexane, and ethanol-acetone mixture) of different polarity. Results demonstrated that the median inhibitory concentration (IC_{50}) of the plant extracts depend on the type of solvents and concentrations utilized. This means that different extracts of CPHs is a potent antioxidant agent and demonstrated inhibition against α-glucosidase however its efficacy was significantly lower when compared to the positive control ascorbic acid and acarbose, respectively.

Keywords: Theobroma cacao, Cacao Pod Husks, Phtyochemicals, α-Glucosidase, Antioxidant

Conclusions

The overall results of this study suggest that CPHs a by-product of cocoa production is a potent antioxidant and demonstrated inhibition against α-glucosidase. This means CPHs could be a valuable source of phytochemicals, mineral and has the potential to serve as alternative herbal supplement against hyperglycemia.

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Functionalized coated magnetic nanopartcicles for lead removal

★★★

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Abstract

In recent years, nanoscience and technology has introduced a new dimension to sciences and technology sectors due to its ability to exhibit super functional properties of materials at nano-dimensions. There is a remarkable rise in research and development in most of countries pertaining to this field [1]**.** These sciences play major role in the development of innovative methods to substitute existing production equipment and to reformulate new materials with improved performance resulting in less consumption of energy and materials and reduceing harm to the environment as well as environmental remediation [2]. Metal nanostructures with functional properties have been studied extensively and there has been a special interest in new magnetic nanosized materials. Magnetic nanoparticles (MNPs) is an emerging field of study and has gained much attention among researchers due to their widespread applications in various fields including catalysis, data storage, magnetic fluids, electronic communication and biomedicine, environmental remediation, etc [3]. Among the magnetic nanosized materials, metal oxides like iron oxide (magnetite, Fe_3O_4 and maghemite, γ-Fe_2O_3) are the most popular and widely used in the field of environmental remediation due to their ease of surface modification, synthesis and low toxicity [4,5]. In addition MNPs exhibit high surface to volume ratios, depending on the particle size, can show enhanced capacity for uptake in water treatment procedures [6]However, an unavoidable problem associated with particles in this size range is their intrinsic instability over longer periods of time. Particles in this size range tend to form agglomerates to reduce the energy associated with the high surface area to volume ratio of the nanosized particles. Moreover, naked metallic nanoparticles are chemically highly active and are easily oxidized in air, resulting generally in loss of magnetism and dispersibility. For many applications it is thus crucial to develop protection strategies to chemically stabilize the naked magnetic nanoparticles against degradation during or after the synthesis [7]. Therefore, a suitable coating is essential to overcome such limitations [3]. Magnetic nanoparticles were synthesized by hydrolysis method. MNPs were coated with polyethylenimine (MNPs-PEI) onto the surface of the MNPs following the reported procedure**.** The surface of MNPs-PEI was modified with various functionalized moieties. The synthesized nanomaterials were characterized by FT-IR, UV, TGA, XRD, HRSEM and HR-TEM. The adsorption capacity of the synthesized nanoadsorbents for the removal of lead was evaluated using Atomic Absorption Spectrometry (AAS). We have also investigated the kinetics, isotherm and thermodynamic studies of the adsorption process occurred. The particles size of the produced nanoparticles were found to be cubic in shape with ~24nm. The optimized conditions for higher adsorption at room temperature were found to be at pH 6.5 and 10mg of absorbent for 50 ml of solution of 25ppm Pb^{2+}.

Keywords: Magnetic nanoparticles, adsorption, water treatment.

Acknowledgments: Organization for Women in Science for the Developing World (OWSD), the University of the Western Cape (UWC).

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Synthesis and Characterization of New Molecularly Imprinted Polymers for Melatonin Delivery

★★★

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Abstract

In recent years, molecular imprinting technology (MIT) as a technique of highly cross-linked polymers syntheses has attracted significant interest in research activity. These polymers capable of specific recognition of the template molecule are called molecularly imprinted polymers (MIPs) and their synthesis, purification, and testing require attention and precision [1]. This research is focused on the area of drug delivery, emphasizing specifically melatonin delivery, as the greatest challenge for MIPs among other applications [1], [2], [3]. Melatonin is a neurohormone produced primarily by the pineal gland at night time [4]. When administered as a drug, it ameliorates many health conditions, particularly insomnia [5], but the drawback is its orally and intravenously fast-release [6]. The safety issue invokes important remarks regarding the clinical applications of MIPs as drug delivery systems as they are predominantly synthesized in organic solvents which may cause cellular damages [5], [2]. To overcome the toxic effects, our work comprises the green synthesis of a series of dextrin-based MIPs-Nanosponges (NSs) using the commonest preparation method of MIPs and NSs. MIPs-NSs were successfully synthesized by mixing, in different molar ratios, the dextrins used as functional monomer, citric acid as cross-linker, sodium hypophosphite monohydrate as a catalyst and distilled water as the solvent. Alongside these, melatonin is the template molecule. The reaction was carried out under vacuum at specific temperatures and times. The resulted polymers were characterized by elemental (EA), FTIR spectrophotometric, thermogravimetric (TGA), differential scanning calorimetry (DSC), and HPLC – UV analyses. This study yielded green synthesized MIPs-NSs with a high encapsulation efficiency of melatonin and able to prolong and control the release of melatonin in pH 7.4 phosphate buffer solution for several hours. No degradation of melatonin was observed during the storage of MIPs-NSs at room temperature and their exposure to the light for several weeks. The work was also compared with non-molecularly imprinted polymers (NIPs)-NSs. To summarize, this research aims to gain advantages over fast-released oral and intravenous melatonin [6], by utilizing MIPs-NSs for its transdermal delivery.

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Preconcentration of bisphenol S and bisphenol F from food samples using dummy molecularly imprinted polymer (DMIP)

* * *

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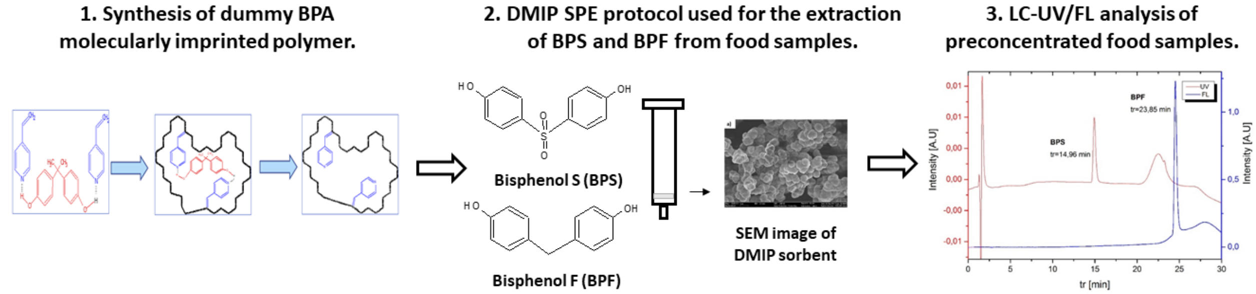
Abstract

For many years bisphenol A (BPA) has been used in the production of plastics or internal coatings of cans [1]. It gains much attention as it occurs to be a dangerous endocrine disruptor which may migrate from plastic containers to food. Due to many restrictions regarding the application of BPA [2], packaging industries started to use other bisphenols (e.g. bisphenol S and bisphenol F) with similar chemical properties to BPA and also identical or even greater toxicity. Due to these facts, when evaluating the safety of compounds for consumer use it is essential to consider the entire classes instead of individual compounds. Since food samples have a complex matrix and the concentration of bisphenols in food is very low, it is necessary to apply clean-up steps to eliminate interfering compounds before analysis, but also preconcentrate the analytes.

The aim of our work was to develop an analytical procedure for selective extraction, preconcentration and determination of bisphenol S and bisphenol F in food samples. In this work dummy molecularly imprinted polymer (DMIP) for solid-phase extraction (SPE) has been successfully prepared and bisphenols were determined by high-performance liquid chromatography with fluorescence and UV detection (LC-UV/FL). By applying SPE with DMIP sorbent prior to LC-UV/FL, the limits of detection achieved in food samples can be lowered to 0.5 ng·g^{-1} for BPF and 5 ng·g^{-1} for BPS. Only 5 mg of DMIP sorbent was sufficient to achieve good recoveries (71 - 113 %) for the analyzed liquid food samples spiked at two concentration levels 0.25 mg·L^{-1} and 0.40 mg·L^{-1}. The analytical characterisation of the proposed method makes it suitable for monitoring programs, intended for the assessment of human exposure to bisphenols in food samples, without using much expensive mass spectrometry detection.



Scheme 1. SPE-DMIP procedure for the preconcentration and determination of bisphenol S and bisphenol F in food.

Keywords

bisphenols, food contamination, solid-phase extraction

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Long-term stable infant formula – conceptual product design study

★★★

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Abstract

Infant formula is an alternative food for babies who do not always receive their nourishment by breastfeeding. Although infant formulas are tailored to fulfil the nutritional requirements of the growing babies, they can also pose health risks for babies because of their high susceptibility to biological contamination. In this context, this project focuses on the design of a novel infant formula that is safer for babies to consume, even in the mentioned conditions. The project aims to design a cost-effective, tasty infant formula that suppresses harmful bacterial contamination and growth over the whole product lifetime, even in tropical conditions. The latter occurs in the target market: the southeast Asia region. With this information in mind, a literature and patent search are performed to better understand the state of the art regarding infant formula, bacteria contamination sources and the characteristics of two main microorganisms that affect the product: Cronobacter Sakazakii and Salmonella Enterica. Next, creativity methods are used to find product concepts that solve the design issue. The generated ideas mainly focus on (1) the product formulation and (2) the processing of the product to achieve the desired specs. On these grounds, the ideas are evaluated and the best performing ones are analyzed, combined and further developed in the following design levels. The chosen superior design is a combination of adding organic acids and garlic derivatives to the formulation, plus using pulsed electric field (PEF) pasteurization in the production process. This way, the product performance on the grounds of bacterial control in production, storage and digestive tract are boosted. On the account of the possibilities of off-flavour from the additives, it is recommended to perform descriptive sensory analysis to detect the presence of undesired flavours. Concerns related to the compliance of the designed product with international regulations, as well as safety confirmations pose no issues with the infant formula solution. For the production of the designed infant formula, a preliminary process plant is proposed. Because of the economies of scale, it should produce 40 kton/yr, and, to be competitive in a globalized market, it should be located in India. Besides, a SHEETS analysis is performed and concludes that, safety wise, the production facilities will need to consider various hazards such as those related to the handling of powders and the works in confined spaces. Regarding the health aspects, it must be clarified that even though the formula will help prevent the illnesses caused by harmful bacteria, medical supervision of the baby is still advised. In this way, the infants and their caretakers will benefit, and the burden on local health systems might be improved, thus having a positive impact on society. For what concerns the technology, improvements have been done in the introduction of PEF pasteurization since it grants more efficiency, a safer product from a bacteriological point of view and improved flavour profile. Regarding the economic feasibility of the design, it is shown that the novel formula's cost will increase in about 3%, slightly lowering the earnings without jeopardizing the product's profitability. A more careful economic analysis must be performed in the future when actual facilities are designed to determine the expected rate of return of the project. The same recommendation applies for the environmental effects of the product, outside the scope of this project.

Keywords
Bacterial control, infant formula, food stability

Acknowledgements
The conceptual design study was contributed by Carolina Carrillo Diaz and Alessandro Endrighi. The packaging conceptual design from Chaitanya Joglekar, Hassan Nagra and Yashi Xiao also dedicated and fulfilled the design project. The design coach, Pieter Swinkels, offered practical and useful design recommendations and suggestions.

Polysaccharide-derived materials for greener destruction of organophosphates

★★★

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Abstract

Herein we present a successful approach of covalent functionalization of polysaccharides (PS) with nucleophilic groups and its application in organophosphates (OP) degradation. PS are cheap, biocompatible and available worldwide in different forms. Moreover, covalent functionalization of PS can improve and add new properties to these materials, expanding the field of application [1]. Thus, covalent functionalization of PS with nucleophilic groups such as imidazole [2-3], present in active sites of enzymes, or alpha-nucleophiles [4], nucleophiles with an improved nucleophilificity due to alpha effect, *e.g.* hydroxamic acids and amidoximes, give PS the possibility to be used as catalyst in nucleophilic reaction. Dephosphorylation reactions are example of important reactions which demand catalysis: OP are toxic and stable and broadly used as pesticides and war weapons. Hence, in our group the raw materials of rice husk (RH) and gum arabic (GA) were functionalized with the nucleophilic groups imidazole, hydroxamic acid or amidoximes under green methodologies giving biocatalysts in solid and colloidal phase which were studied in the degradation of OP [2-3]. The RH, GA and derived biocatalysts were characterized and modification proven by Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR) of ^{13}C, potentiometric titrations and among other techniques [2-3]. The biocatalysts were studied in the dephosphorylation reaction of substrate diethyl 2,4-dinitrophenyl phosphate (DEDNPP) and pesticide Paraoxon. The catalytic increments of the biocatalysts were in the order of 10^5-10^7 with DEDNPP and in the order of 10^4-10^7 with the pesticide Paraoxon, under mild reaction conditions: room pressure and temperature, aqueous medium, pH close to neutral, etc [2-3]. Moreover, the biocatalysts presented recyclability over sequential cycles of catalysis and selectivity in the nucleophilic attack towards the phosphorus atom. Furthermore, the remarkable catalytic performance of the biocatalysts with the studied OP suggests that they probably can have similar reactivity with other OP. The catalytic increments are between the highest reported in literature for the reaction with the OP DEDNPP and Paraoxon. We highlight the fact that the biocatalysts were synthetized from sustainable and inexpensive sources of PS using green methodologies for the degradation of OP, an innovative and efficient approach to degrade pesticides using green chemistry and sustainable materials. Moreover, the applicability of the synthetized materials can be expanded to other fields as environment remediation, emerging contaminants sensing and scavenging and biocompatible materials for medicine.

Keywords: Pesticides, nucleophiles, catalysis.

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The use of the biotechnology to resolve the contamination of soils and water

★★★

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Abstract

Economic strength of most countries is based on the agricultural and industrial sectors which itself depends on logistics. Logistics is a rapidly developing sector of activity and mobility is essential to our lifestyles. At the same time, the transport sector is the main source of environmental pollution, mainly for the marine ecosystem, because petroleum freight accounts for almost a third of world maritime trade which is the main offender of marine pollution problem. Oil spills, the most serious environmental hazard, affect marine life both offshore and along the coast. Oil is the cause of pollution, as well as the destruction of fauna and flora. However, as not to forget the other party in the difficult problem, which is pesticides and according to the United Nations (UN) [1] the world population expected to reach 8.5 billion in 2030, 9.7 billion in 2050 and exceed 11 billion in 2100, the enormous demographic growth is one of the causes of the intensive agriculture, which leads to the use of chemical inputs such as pesticides. In light of these data, are there any strategies or solutions that can mitigate or even completely eliminate the impacts of pesticide use? Yes, the biotechnology strategies, which are based on the bioremediation of soils and water contaminated by the use of ecological solutions depend on rhizobacteria selected through their ability to resist and degrade these chemical inputs. Moreover, biodegradation is considered to be the ultimate step in removing hydrocarbons from the marine environment and pesticides in agricultural soils. Likewise, seawater contains a wide range of microorganisms that use hydrocarbons as a source of carbon and energy. They can partially or completely degrade oils into water-soluble compounds or carbon dioxide and water. In addition, it's not strange that seawater content microorganisms like soil that has a very important role in biodegradation. The proposed research is focused on the development and optimization of innovative bioremediation processes (biostimulation and/or bioaugmentation) to be applied for the recovery of areas contaminated by pesticides and hydrocarbons. By the same token, Improvement, and updating of experimental protocols, making new methods of analysis available to future researchers and enriching the bacterial bank.

Keywords: Bioremediation, Pesticides, Hydrocarbons.

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The Complexation Of Oxyresveratrol In Cyclodextrin Based Nanosponges Complexes Enhances Bioactivities And Protection

★★★

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Abstract:

The complexation of the bioactive compound oxyresveratrol (OXY) with a polymer called cyclodextrin-based nanosponge (CD-NS) and its application was studied [1]. A new methodology is used to calculate, an apparent inclusion complex constant (K_{Fapp}) between a ligand and CD-NSs. Moreover, the K_{Fapp} of resveratrol was also evaluated and compared. The complex of OXY with the nanosponge β-CDI 1:4, was studied *in vitro* using DSC, TGA and FTIR techniques and its drug loading and release behavior were studied. An *in vitro* digestion showed higher protection of OXY complexed than free OXY. The bioactivity enhancing capacity of OXY was also studied against prostate (PC-3) and colon (HT-29 and HCT-116) cancer cell lines, where it showed stronger cell viability inhibition than the free drug. The findings as a whole represent a new opportunity for studying the complexation of drugs in CD-NSs and the use of oxyresveratrol as an ingredient in nutraceutical products.

Keywords: Oxyresveratrol; nanosponges; cyclodextrins.

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Facile removal of fluoride ions from water using triethylamine modified polyethylene adsorbent

★★★

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Abstract

Highly fluoridated water is hazardous to human and animal health and effects are not limited to dental and skeletal fluorosis, diarrhea and impaired brain development. Traditional water treatment methods have limitations such as high production cost, ineffectiveness and are not reusable. In this work, the use of waste polyethylene materials derived from municipal solid waste as a green water treatment technique that affords low price, value addition and ecological friendly technology has been presented. The polyethylene wastes were dispersed in vegetable oil and modified using triethylamine. Modification was confirmed by Fourier transform infrared spectrometry (FTIR). The effect of pH initial equilibrium time, concentration and adsorbent dose were investigated and optimized. Sorption was found to prescribe to Langmuir adsorption with an adsorption capacity of 10. 30 mgg^{-1}. The removal process was found to be optimal at pH 6.0. This study showed that triethylamine modified plastic material has a potential application for removal of fluoride from contaminated water.

Keywords: Adsorption capacity, triethylamine, vegetable oil, kinetic isotherm

Surface modification of titanium oxide as a support of metal nanoparticles for solar driven water splitting to produce hydrogen

★★★

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Abstract

Solar energy is an inexhaustible, clean and renewable natural resource, and the sunlight reaching the Earth's surface on an hourly basis exceeds the annual global energy consumption. Efficient utilization of solar energy requires that this energy be converted and stored in a cost-effective and environmentally benign fashion. Hydrogen a unique zero-emission energy carrier. Overall water splitting using solar light and particulate photocatalysts has been considered as a low-cost technology with the potential to enable large-scale solar hydrogen production, because of the ready synthesis of the associated photocatalysts as well as the simple reactor and facility designs. The position of the CB and VB of TiO_2 is larger than 1.23 eV width which corresponds to the water splitting potential making TiO_2 one of the apt materials for water splitting. However, there are other issues which affect the efficiency of water splitting on TiO_2, such as high recombination rate and the wide band gap which permits absorption of only UV light. Since UV light comprises only 4% of the solar spectrum, modification of the conventional support (aeroxide) using both hydrolysis and sol gel processes and incorporation of nanoparticles (Au and Pt) in order to reduce electron-hole recombination is an alternative to increase the efficiency of catalytic activity of TiO_2. Modified TiO_2 will be synthesized by combining a hydrolysis process of titanium (IV) butoxide with sol-gel on the surface of the aeroxide. The aeroxide will be dried and dispersed in de-ionized water under vigorous stirring and titanium (IV) butoxide added until Ti-precursor sol has formed. The obtained dry solid will be added and crushed into a fine powder. The photocatalysts will be obtained using deposition-precipitation with urea. Chloroplatinic acid hydrate and gold (III) chloride hydrate will be used as precursors of Pt and Au. The modified support will be dispersed in a urea solution and the parent solution added in different concentrations. The suspension will be aged, centrifugated and dried. The crystalline phases will be determined using an x-ray diffractometer. The average particle size diameter will be obtained from the transmission electron microscope data while the absorption spectra will be obtained by using ultraviolet-visible reflectance spectroscopy. A hydrogen production test will then be conducted. The hydrogen production test will be used to determine which specific surface modification of the support produces the highest hydrogen production rate.

Keywords: Water splitting, surface modification, hydrogen production

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Effect Of Eucalyptus Oil On Reduction Of Bacterial Growth In Drinking Water

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Abstract

The general objective of this research is to use essential oil from eucalyptus citriodora as disinfectant to reduce bacteria in drinking water as much as green chemistry in comparison with the use of Chlorine for the same purpose. Water is acting as life line for living organisms on the Earth, without that no life. Due to global industrialization, availability of pure water is one of the major issues. Also effluents are directly or indirectly discharged through the river stream, which affect the ground and surface water. In Rwanda many water treatment plants use Chlorine as disinfectant which is highly expensive and its high concentration is carcinogenic. Many plants and herbs are used as antimicrobial due to its properties of destroying cell membrane of bacteria. In this regard eucalyptus extracted oil was used as antibacterial agent to treat the drinking water. In this research, firstly we were checking the untreated water if they had total coliforms, after seeing that we were using 1.5 up to 5ml of essential oil this helped us to precisely the oil needed where the efficiency vary from 39.06% up to 99.8%. So that we recommend that there would be further research on specific species of total coliform bacteria and their biochemical characteristics and do comparison of efficiency between choline and essential oil.

Keywords: Green chemistry, Essential oil, Bacteria.

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Testing the Inclusion Complexes of Oxyresveratrol and β-Cyclodextrin in Juice and Milk Food Models

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Abstract

Food industry is constantly searching for novel foods enriched in bioactive compounds in order to stand out from the competition. However, most of the functional foods that can be found in supermarkets are fortified with the same bioactive ingredients, leading to a stagnant market. For that reason, interest in researching novel and different molecules with beneficial health effects as antioxidant and anticancer agents is increasing. In the present study, oxyresveratrol, a biologically active stilbene, is encapsulated in β-cyclodextrin (β-CD) to enhance its physicochemical properties before being incorporated into food models of juice and milk. Cyclodextrin selection was performed according to the characterization of the complexes with α-CD, β-CD and γ-CD by SEM, DSC, TGA and molecular docking. These food models were maintained under typical storage conditions (darkness and/or refrigerated) for one month and, their stability was evaluated by measuring ºBrix, pH and UV-Vis spectra. The effect of encapsulation on the solubility and antioxidant activity of oxyresveratrol was also analysed. The results indicated that the food models were stable for at least five weeks and that cyclodextrin supplementation leads to a higher concentration and antioxidant capacity of the bioactive compound than when it is not used. These findings may be interesting for industries to design functional foods enriched in oxyresveratrol.

Keywords: Oxyresveratrol; Cyclodextrins; Food Model

Topic: Food Safety

Acknowledgments: Fundación Séneca - Agencia de Ciencia y Tecnología de la Región de Murcia

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Phytochemical Screening and Antimicrobial Properties of the stem of Nuclea pobeguinii

★★★

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Abstract

Nauclea pobeguinii is one of the species of *Nauclea* genus from the family of Rubiaceae which are known for their medicinal values. The extraction of bioactive constituents of *N. pobeguinii* was done using solvents of different polarities (n-hexane, ethyl acetate and ethanol). The cold method of extraction was employed by carrying out serial exhaustive extraction on the stem sample after drying and reducing the sample size through pulverization. From the photochemical analysis of the concentrated crude extract obtained, alkaloids, tannins, flavonoids, steroids, saponins and glycoside were observed to absent in the n-hexane extract, while all the above mentioned secondary metabolites with exception of glycoside were observed to be present in the ethyl acetate and ethanol extracts. The antimicrobial studies of the ethyl acetate and ethanol extracts shows inhibitory activity on Gram-negative (Escherichia coli, Klebsiellapneumoniae, Salmonella typhimurium Pseudomonas aeruginosa and proteus mirabilis) and Gram-positive (Staphylococcus aureus and Streptococcusagalactiae) with zone of inhibition of 8-20mm except for n-hexane which shows no inhibitory. This invariable shows that ethyl acetate and ethanol extract of *N. pobeguinii* possesses antimicrobial properties for the treatment of various ailments (diarrhea, thyphoid, fever and as an antiseptic agent).

Keywords

Nuclea pobeguinii, Rubiaceae, extraction, phytochemicals, antimicrobial activities

Acknowledgements

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Production and formulation of an ecological mixed fertilizer based on rock phosphate and plant growth promoting bacteria

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Abstract

The current agricultural practices are based on the massive use of synthetic chemical pesticides which have harmful impacts. The use of rock phosphate (RP) as natural phosphatic fertilizer and plant growth promoting bacteria (PGPB) could be an alternative approach. PGPB are key players in crop productivity and bioremediation of different types of pollutants (i.e. pesticides, heavy metals, hydrocarbons, explosives...) [1-5].

The main objective of my thesis project is to produce and formulate an ecological mixed fertilizer based on RP and PGPB. The specific objectives of the study are: (i)the physico-chemical and microbiological characterization of Tunisian RP; (ii)the screening of extremophilic bacterial collections and selection of high RP-solubilizing PGPB; (iii)the formulation and optimization of the composition of the mixed ecological fertilizer using mixture designs and response surface methodology and (iv) the study of RP solubilization mechanisms by selected PGPB and evaluation of their bioremediation potential against heavy metals and radionuclides.The agricultural efficiency of mixed fertilizers will be validated and evaluated in potato, wheat and corn fields by measuring plant growth parameters and yield promotion. Different plots will be used as controls (plots without fertilization, with standard fertilization, with RP only and with PGPB).

Keywords

Sustainable agriculture, ecological fertilizers, biocatalysts, rock phosphate, phosphate solubilizing bacteria, phosphatase.

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Adsorptive Removal Of Methylene Blue Dye Using A Novel Hybrid Polymer Hydrogel Containing Activated Carbon Or Tio2 Nanoparticles

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Abstract

Organic dyes present in industrial wastewater pose serious threats to public health and the environment. These eco-toxic contaminants must be treated to bring their concentration in accordance with the Brazilian legislation. Adsorption is the most widely utilized process due to high efficiency, simple procedure and cost effectiveness. Herein, superabsorbent polymer (SAP) hydrogels and their composites were prepared, with the incorporation of activated carbon (SAP-AC) or TiO2 nanoparticles (SAP-TiO2). A continuous up-flow fixed bed column (6 cm internal diameter and 30 cm in length) reactor having 70 mg of dried composite adsorbent was fed with 300 mL of methylene blue (MB) (50 ppm) using a peristaltic pump. The adsorption process was maintained for 24 h, and small sample aliquots (5 mL) were collected at definite time intervals and analyzed using a UV-Vis. spectrophotometer (λmax = 665 nm) for the residual MB concentration. It was observed that the pH and temperature have marked effects on MB adsorption and the swelling ratio of the composite. Comparatively, maximum MB adsorption was recorded (98.3%) with 305.9 g g-1 swelling capacity and reaching the maximum MB adsorption equilibrium (213.2 mg g-1) using SAP-AC at pH 6.0 and 37.5 °C. For pH 2 and 37.5 °C, the lowest swelling capacity was found, i.e., 9.57 g g-1 for SAP-AC and 7.62 g g-1 for SAP-TiO2, respectively. Furthermore for the same conditions, the MB adsorption capacity and the residual MB concentration were found to be 45% and 27.5 ppm (qe = 94.0 mg g-1), respectively, using SAP-AC; for SAP-TiO2, 22.8% and 38.6 ppm (qe = 48.1 mg g-1) were attained, respectively. The current study has proved that the synthesized SAP composites show good activity and selectivity for the deep adsorption of MB.

Keywords: Superabsorbent polymers; Adsorption; Organic dyes

Nitrification Characteristics Of Nitrite To Nitrate For Nitrogen Removal And Nitrous Emission

★★★

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Abstract

Nitrate mainly originated by fertilizers and nitrification is essential pollutant of ground water and surface water. It has a big effect on human health and environment. The oxidation of ammonium and nitrite play a key role to generate nitrate. The nitrification process can be affected by several factors, leading to the formation of undesirable end products as NO_2^- and N_2O. The fresh leachate collected and investigated has shown that NO_3-N and NO_2-N less than 0.1 mg/L, while the BOD5/TN ratio seems to be at risk for nitrous emission. In this study, the aerobic and anaerobic operation method has applied, the rate of nitrous during five days increased remarkably after 2nd day of biochemical incubation in sealed bottles. The concentration of nitrous oxide gas was measured by gas chromatography.

Keywords: Nitrification, nitrate, nitrite, nitrogen, nitrous emission

Contribution Of Tartaric Acid To The Free Radical Scavenging Activity Of Ascorbic Acid

★★

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Abstract

Tartaric acid (AT) is an organic acid found in grapes and wines [1] and known as a good preventive antioxidant and a metal chelating agent [2], used to ameliorate the quality of grape products. To prevent the oxidation of the colored and organoleptic fractions of musts, juices and wines, ascorbic acid (AA) is also used in oenology [3]. However, less information is provided about the synergistic [4] influence of AT on the free radical scavenging activity of common antioxidants like AA. In this study, the contribution of different concentrations of tartaric acid on the antioxidant activity of ascorbic acid (AA), tested through the DPPH assay, is presented. Three different mixtures of AA – AT showed a significant synergistic effect of 1.20, 1.17 and 1.13. With the increase of AA and TA concentrations, the additive effect (1, 0.99 and 0.91) was noticed. Thereby, the results suggested that the synergistic effect is dependent on concentrations of both organic acids.

Tables and Figures

Table 1. Synergistic effect and inhibition percentages for mixtures of ascorbic and tartaric acid.

Concentration of AA	TA$_1$ 22.3×10^{-3} M		TA$_2$ 67×10^{-3} M		Synergetic Effect	
	%$I_{mixture}$	%$I_{theoretical}$	%$I_{mixture}$	%$I_{theoretical}$	TA$_1$	TA$_2$
AA$_1$ 15×10^{-6} M	39.0	32.4	38.6	34.2	1.20	1.13
AA$_2$ 22,5×10^{-6} M	58.3	49.8	46.6	51.1	1.17	0.91
AA$_3$ 45×10^{-6} M	95.9	96	95.6	96.1	1	0,99

Keywords

Tartaric acid, ascorbic acid, DPPH method, synergism

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5. CLIMATE CHANGE DAMAGES MITIGATION

Catalyst development for the conversion of renewable carbon sources and energy - overcoming the fossil-based economy

★★★

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Abstract

Our global economy is based on fossil raw materials. Renewable carbon sources like biomass and CO_2 on the one hand and renewable energies such as wind, solar and waterpower represent alternative sources (Fig. 1). CO_2 can be converted to value-added C_1-chemicals like methanol and formaldehyde. An example for the valorization of biomass is the selective hydrogenolysis of polyols. To store renewable energies, hydrogen production by water electrolysis is an important reaction, which needs to be optimized. All these three reactions are current research topics, which our group is dealing with. We are aiming to develop heterogeneous catalysts for application in the field of green chemistry.

To produce formaldehyde from carbon monoxide (and later carbon dioxide) we are working on the development of bimetallic catalysts on various supports. To enhance activity and selectivity the choice of solvent and catalyst is highly important [1]. For the hydrogenolysis of poyols the heterogeneous catalyst was optimised by tuning the electronic properties of the metal nanoparticles by variation of the support material [2]. Additionally, the influence of a basic co-catalyst on activity and selectivity was investigated revealing a stabilising effect of the cation on transition states. Metal-free carbon-based electrode materials were designed to catalyse the oxygen evolution reaction of the electrochemical water splitting [3]. Here a good balance between hydrophilicity and conductivity is required to reach an optimal performance of the catalyst.

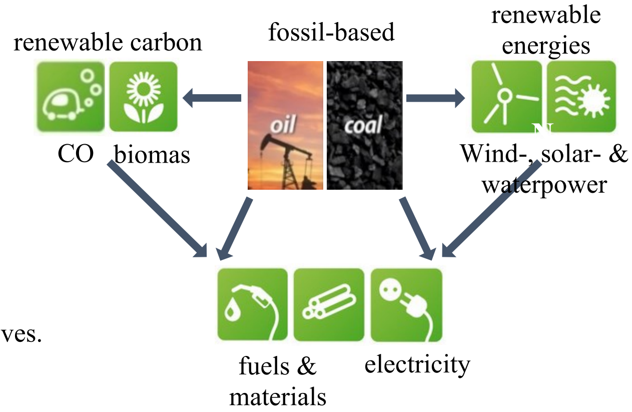

Figure 1: The production of fuels, materials and electricity based on fossil resources and possible alternatives.

Keywords: Carbon dioxide, Hydrogenolysis, water splitting, oxygen evolution reaction, heterogeneous catalysis

Acknowledgements

We thank the DAAD and the Max Planck society for financial support.

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CO_2 electroreduction: Enhanced activation and selectivity by ionic microhabitat

★★★

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Abstract

In the past hundreds of years, the unrestrained combustion of non-renewable fossil fuels leads to a continuously rising level of atmospheric carbon dioxide (CO_2), which has created serious issues. Meanwhile, CO_2 is also a cheap, abundant and renewable C1-feedstock that can be converted into useful chemicals. Electrochemical CO_2 reduction reaction (CO_2RR) is one of the most promising ways to conversion CO_2 [1]. However, the low solubility of CO_2 and complicated reaction process in aqueous solution render CO_2RR inefficient. Recently, ionic liquid (IL) has been proven to be a hoping reaction medium for CO_2 electrochemical reaction because of its unique physicochemical properties [2].

Herein, high efficiency of CO_2 capture and conversion is achieved via ionic microhabitat (IMH) based on the novel ILs. The IMH not only activates CO_2, but also provides a facile route for the transferring of the activated CO_2^- to the cathode surface, which improve both selectivity and current density of target products. A high HCOOH Faradaic efficiency of 95.2% with 24.5 mA cm^{-2} partial current density was abtained in the IMH based on the novel superbase IL 1-butyl-3-methylimidazolium 1,2,4-triazolide ([Bmim][124Triz]) [3]. The experiments and calculation demonstrated that the nanoscale aggregates and chemical interaction in the ion of [124Triz]-CO_2^- result in a superior solubility of CO_2 under ambient conditions and the stable CO_2 molecule is changed to a bent form in the [124Triz]-CO_2^- ion, which is favorable for CO_2 activation and CO_2^- stabilization. Moreover, CO_2 can also be converted into oxalic acid ($H_2C_2O_4$) in the other IMH based on the novel aprotic aromatic ester-functionalized IL and a high $H_2C_2O_4$ FE of 86% with formation rate of 168.4 μmol cm^{-2} h^{-1} was obtained. The results of calculations indicated that high efficiency of CO_2 dissolution, activation, and conversion are achieved *via* bis-active sites of novel IL in the IMH. It can be seen that the novel IL offers a low energy and high selective pathway for CO_2 electroconversion through an IMH.

Keywords

CO_2 conversion, Ionic liquid, Ionic microhabitat, Electroreduction

Acknowledgements

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Design, synthesis and characterization of new PGM-based half-sandwich complexes for CO_2 hydrogenation to formates and *N,N*-diethylformamide

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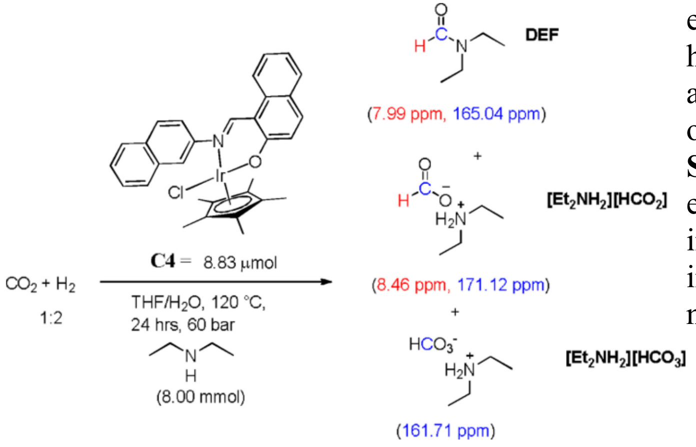
Abstract

The valorization of carbon dioxide (CO_2) as a non-toxic alternative one-carbon (C1) synthon to carbon monoxide and phosgene for the synthesis of organic chemicals and fuels is of interest in homogeneous catalysis.[1],[2] The transition metals ruthenium and iridium have been reported to afford maximum turnover numbers of CO_2 hydrogenation under mild catalytic conditions.[1]-[4] Herein, we present new *N,O*-coordinated Ir(III), Rh(III), Ru(II), and Os(II) half-sandwich complexes **C1** – **C4** that have been designed, synthesized, and applied as homogeneous pre-catalysts in the experiments for direct and indirect CO_2 hydrogenation under basic conditions. In the presence of DBU, the Os(II) half-sandwich complex gave a TON of 889 for [DBUH][HCO_2] formation under a partial pressure of 60 bar CO_2/H_2 at 120 °C assisted by heterogeneous side reactions. The Rh(III) and Ir(III) half-sandwich complexes exhibited a great efficiency in the homogeneous hydrogenation of carbon dioxide to afford formate and *N,N*-diethylformamide (DEF) in the presence of DBU and diethylamine, respectively. Following **Scheme 1**, the group 9 half-sandwich complexes eminently qualify as useful in the direct and indirect hydrogenation of CO_2 to afford reaction intermediates that can be used to make carbon-neutral fuel.[5]



Scheme 8: Catalytic transformation of carbon dioxide by Ir(III) half-sandwich complex **C4** to form formate adduct, *N,N*-diethylformamide(DEF),and residual bicarbonate.[5]

Keywords

CO_2 hydrogenation; Iridium(III); Rhodium(III); Osmium(II); Ruthenium(II); Formamide; Formate

Acknowledgements

SASOL SA, the National Research Foundation, South Africa, (Grant number 117989), and the University of Johannesburg Centre for Synthesis and Catalysis are greatly appreciated for this research.

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Development Of New Homogenous Catalysts For Co_2 Reduction To Formates

★★

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Abstract

The huge consumption of fossil resources and the resulting CO_2 emission has motivated scientists to develop benign and unlimited energy systems based on renewable resources.[1] The increase in energy demand has led to cleaner generation of energy from hydropower, wind and photovoltaic energy. Researchers are now focused on the utilization of carbon dioxide and biomass as a carbon resource for the chemical industry as opposed to the use of fossil reserves.[2] The disadvantage of relying on fossil fuel include: i) depletion of fossil reserves; ii) the negative impact of the current energy production on the environment, specifically the emission of greenhouse gases along with global warming.[3] The hydrogenation of carbon dioxide is a promising process because carbon dioxide is abundant, inexpensive and is C_1 source which is non-toxic, non-flammable and non-corrosive. The utilization of CO_2 requires high energy hence catalysts are required to overcome kinetic and thermodynamic stability.[4, 5, 7] The heterogenous hydrogenation of CO_2 is usually carried out under harsh conditions (high temperatures and pressure) and shows low selectivity and unsatisfactory activity, resulting in extensive energy consumption therefore homogenous hydrogenation is of interest.[6] High catalytic activity for homogenous hydrogenation of carbon dioxide has been widely investigated using complexes of iridium and ruthenium.[7-8] Herein, we investigate the application of new palladium pincer complexes in the hydrogenation of carbon dioxide to formate (Figure 1).

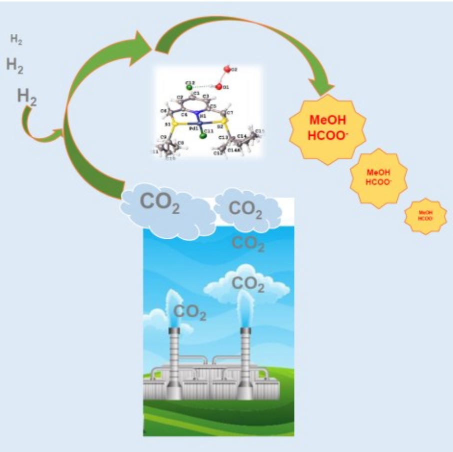

Figure 1: Illustration of CO_2 hydrogenation to formate.

Keywords: hydrogenation, carbon dioxide, palladium, pincers, formats

Acknowledgements: University of Johannesburg, Sasol and NRF

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Estimating net oxygen released by the restored mangrove forests in Southeast Asia

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Abstract

Mangrove release oxygen during photosynthesis. They utilize energy from sunlight to make organic carbon by using carbon dioxide and water. In this process 6 molecules of carbon dioxide are used and 6 molecules of oxygen get released as by-product. To achieve positive net oxygen production, mangrove need to store the fixed organic carbon in their body biomass and underlying soil, reduce the decomposition rates or increase the rate of oxygen production as seen in rapid growing mangrove seedlings. While mangrove restoration efforts have been carried out to aid in carbon sequestration, less attention has been given to the role that these artificial forest play in oxygen production.

We estimated the amount of oxygen released by the restored mangrove forests using the previously reported carbon sequestration rates [1, 2 & 3]. Net oxygen released was determined according to [4]. Results show that the net oxygen release by the restored mangrove forests aged between 8 – 10 years were 4 ± 1.1, 27.1 ± 0.0 and 25.4 ± 0.0 tonnes ha^{-1} y^{-1} at Bali Indonesia, Khanom in Thailand and at a site in Malaysia respectively. These values may be even higher than those reported from their natural counterpart mangrove strands (Table 1).

Table 1: Net O2 release (in tonnes ha-1 y-1) by the restored mangrove forests in Southeast Asia

Location	Author	C sequestration (tonnes ha-1 y^{-1})	Net O_2 Release (tonnes ha-1 y^{-1})
Restored sites			
Bali, Indonesia	Sidik[1]	1.5 ± 0.4	4.0 ± 1.1
Khanom, Thailand	Matsui[2]	8.3± 0.0	22.2 ± 0.0
Malaysia	Sanderman [3]	9.5 ± 0.0	25.4 ± 0.0
Natural sites			
Bali, Indonesia	Sidik[1]	2.2 ± 0.6	5.9 ± 1.6
Sawi Bay, Thailand	Alongi[5]	1.84 – 2.81	4.9 – 7.5
Matang reserve, Malaysia	Alongi[6]	1.48 – 4.1	3.9 - 10.9

Keywords: Restored mangroves, Net oxygen production, Carbon sequestration, Molecules

Acknowledgements: Many thanks to the VLIR-UOS scholarship program that support authors' postgraduate training at Vrije Universiteit Brussel (VUB), Belgium.

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Sustainable Functional Constructs Engineered From Cellulose Nanofibers to Stifle Electromagnetic Pollution

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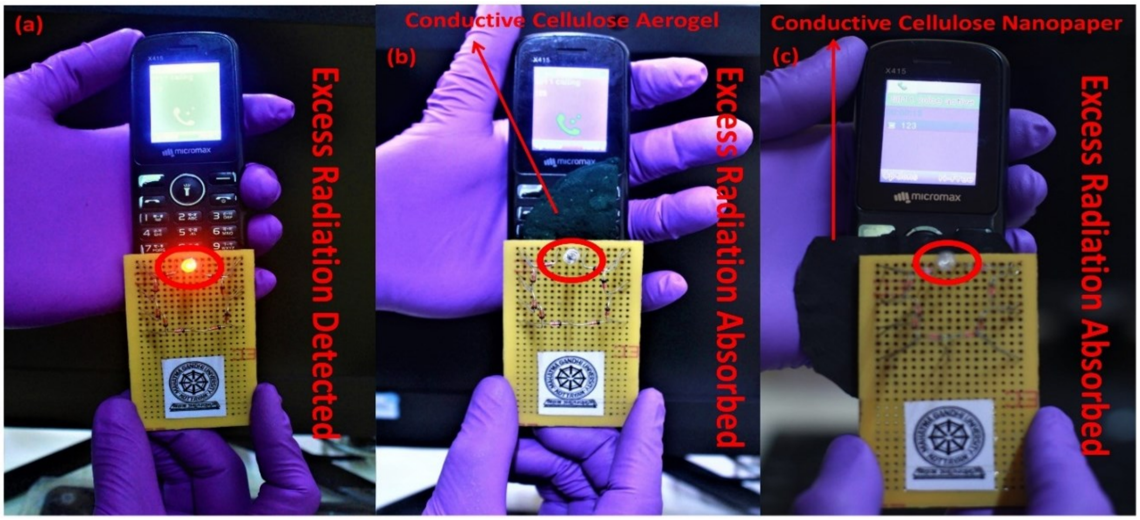
Graphical Abstract



Abstract

Electromagnetic (EM) pollution is ubiquitous and has soared to a great extent in the past few decades. The use of plant sourced cellulose nanofibers (CNF) to fabricate sustainable and high performance electromagnetic shielding materials is foreseen as a green solution by the electronics industry to address this unseen pollutant. Herein, we fabricated a series of functional constructs engineered from CNF viz. flexible nanopapers and highly porous aerogels after *in-situ* polymersing aniline monomer onto the surface of CNF in aqueous medium devoid of any organic solvents [1,2]. These conductive nanopapers and aerogels show tremendous potential for absorbing excess EM radiations emitted out from a mobile phone and can be considered as a sustainable solution to suppress EM pollution.

Keywords: Cellulose Nanofibers (CNF), *In-situ* polymerization, Aerogels, Nanopapers, Electromagnetic Pollution.

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Uncontrolled waste disposal practices in low-income areas

★★★

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Abstract

The first principle of green chemistry recommends waste prevention. This is very important for production processes, but it is also very important in everyday life. The proposed poster focuses on the latter perspective.

Waste is any substance, which the holder discards. 2.01 billion ton of waste is generated worldwide every year, and about 33% of that waste is not properly managed because not all parts of the world have adequate waste collection systems [1]. Efficient waste collection system is regarded as one of the most significant steps in efficient waste management. In low-income areas, most of the waste is either openly burnt or dumped into the land or rivers. There are many factors that contribute to uncontrolled waste disposal practices [1, 2]; they include lack of governmental policy and finance, poor environmental awareness, geographical constrains, low market for recycled materials, lack of long term planning in waste management, resistance to change in terms of separation of waste at the source, lack of regular waste collection services, etc. Mismanaged waste affects our environment and poses a serious threat to public health. It clogs drains, what is particularly dangerous in times of flooding; contaminates the soil, with harms to animals; contaminates rivers and oceans, thus damaging aquatic life; and favours the transmission of diseases.

The growing problem of uncontrolled waste-disposal practices in low-income areas can be tackled by combining traditional and integrated waste management practices. Government programs, local authorities, and civil society need to promote platforms for developing environmental awareness and providing adequate training for proper waste management in low-income areas, taking into account the specific characteristics of each community. Traditional practices such as composting, or recycling options that can be useful for agriculture or for small businesses, need to be encouraged, and the best implementation ways need to be popularised. Practices such as dumping all what cannot go into composting need to be prevented through sufficiently strong campaigns and measure. On the other hand, prevention is possible if waste separation at the source is promoted and accompanied by detailed explanations, and kerbside collection services are made available.

Keywords: Integrated waste management, Low-income areas, Recycling, Waste prevention

Acknowledgements. The authors express their gratitude to the Scientific Committee of the Postgraduate Summer School on Green Chemistry 2020 for providing us the opportunity to present our poster at the conference.

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6. EDUCATION

Teaching Green Chemistry To Deaf Students: A Brazilian Case Study

★★★★

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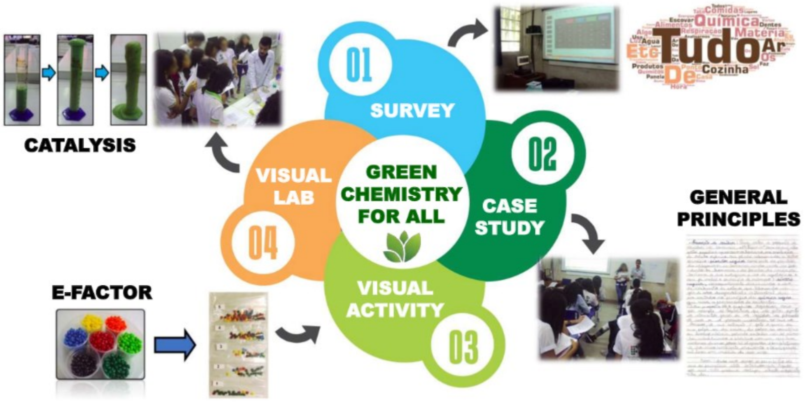
Abstract

In 2020, there are more than 400 million people worldwide have disabling hearing loss, and it is estimated that by 2050 over 900 million people will have deafness[1]. Thousands of these citizens are students who are enrolled in high school and higher education programs in Brazil. Unfortunately, Traditional Chemistry is not particularly inclusive and sustainable. In the context of the Teaching of Chemistry and Environmental Education, Green Chemistry (GC) must be worked on in an integrated, continuous, and permanent way. Thus, the objective of this work was to probe and evaluate, in a general way, the prior knowledge about GC of students of the 1st year of the Technical Course on Environmental Control Integrated to High School of the Federal Institute of Paraiba (IFPB), in Brazil, as well to adapt and develop didactic resources that facilitate the access of hearing and deaf students in this important theme. Methodologically, our work was developed and applied to facilitate the teaching and learning process. The project was divided into four stages: survey questions (1), case study (2), visual-educational activity (3) and (4) experiments. Anastas and others propose that a systems thinking approach is also required for a sustainable future[2]. Results showed that there was a positive impact on the learning of students and a greater interest in the subjects of Chemistry and Introduction to Environmental Education. This case study is a good example to introduce all (hearing and deaf) students to the 12 Principles of GC as well as important general chemistry concepts with a stimulating educational environment[3]. Most importantly discovering new approaches methods to improved access in GC for an effective cultural heritage and global social well-being should be a priority.

Schema 1: Theoretical-practical activities developed during this project.



Keywords: Green Chemistry. Case Study. Inclusion.

Acknowledgements: To students enrolled in this project, CAPES and IFPB for the support.

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POSTER WINNERS AWARDS

83 Posters were received and 60 students had the opportunity to expose their selected posters at the **poster sessions** from Monday 6th July to Thursday 9th July. The poster sessions can be considered a highlight of the Summer School, for the originality and the scientific value of the contributions, for the significant number of young people that shared their researches with the other attendees and for the interest shown by the participants.
During the poster awarding ceremony six participants were awarded for their posters and gave an oral presentation on their work.

The 60 best posters were selected by **a Scientific Jury, composed by the following Members:**
- Neil Coville, *Chairman of the Jury and Emeritus professor of University of the Witwatersrand, Johannesburg, South Africa*
- Ana Aguiar-Ricardo, *Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal*
- Mary Kirchhoff, *Director of the ACS Green Chemistry Institute, Washington DC, USA*
- Gloria Obuzor, *Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria*
- Aurelia Visa, *Romanian Academy "Coriolan Drăgulescu" Institute of Chemistry, Timisoara, Romania*

The 6 winners were:
- Carlos Alberto Da Silva Junior, *University of Campinas (UNICAMP), Brazil*
Teaching Green Chemistry To Deaf Students: A Brazilian Case Study
- Melissa Greta Galloni, *Università degli Studi di Milano, Italy*
Iron functionalised hydroxyapatites as efficient eco-friendly catalysts for air-quality protection
- Tafadzwa Precious Mabate, *University of Johannesburg, South Africa*
Inorganic-Perovskite Catalyzed Transfer Hydrogenation Reaction of Cinnamaldehyde Using Glycerol as a Hydrogen Donor
- Li-Qi Qiu, *Nankai University, P. R. China*
Highly Efficient Visible Light-Driven Rhenium Catalysis for CO2. Reduction through Second-Sphere-Modification Strategy
- Kristy Stanley, *University College Dublin, Ireland*
Effect of Ni NP morphology on catalyst performance in non-thermal plasma-assisted dry reforming of methane
- Kevin Waibel, *Karlsruhe Institute of Technology (KIT), Germany*
A more sustainable and highly practicable synthesis of aliphatic isocyanides

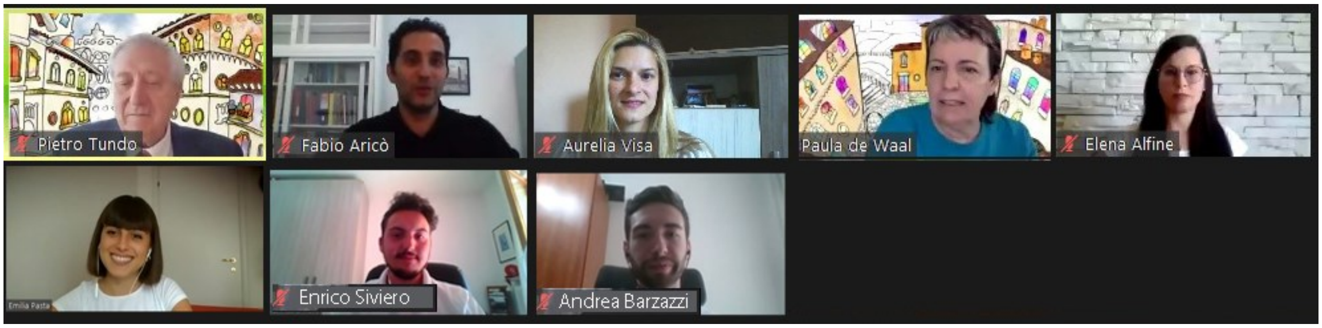
They held a talk on their research of about 10 min each.

The Award consists in an original print of Venice, sent to the winners through postal service.
The prints were purchased from a Bookstore in Venice specialized in antiquities:
https://www.libreriaemiliana.com/

GROUP PHOTO

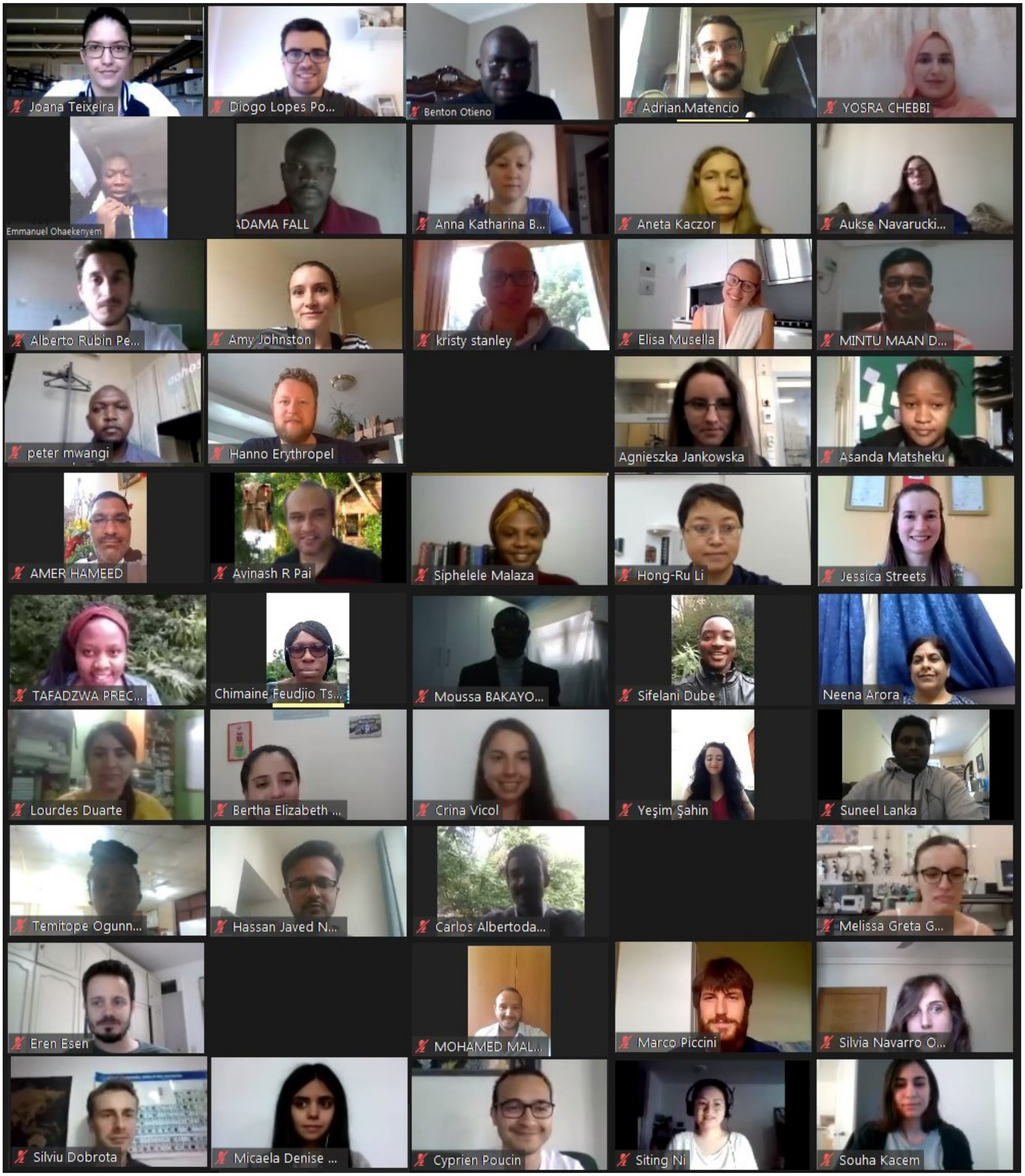
The last day of the Summer School, we asked to all the participants if they would like to be in the group photo of the Green Chemistry Postgraduate Summer School online.
With their consent, we made several screenshots of the Zoom platform, the result is below.

The Organizing Committee



Teachers

Students


Joana Teixeira
Diogo Lopes Po...
Benton Otieno
Adrian.Matencio
YOSRA CHEBBI
Emmanuel Ohaekenyem
ADAMA FALL
Anna Katharina B...
Aneta Kaczor
Aukse Navarucki...
Alberto Rubin Pe...
Amy Johnston
kristy stanley
Elisa Musella
MINTU MAAN D...
peter mwangi
Hanno Erythropel
Agnieszka Jankowska
Asanda Matsheku
AMER HAMEED
Avinash R Pai
Siphelele Malaza
Hong-Ru Li
Jessica Streets
TAFADZWA PREC...
Chimaine Feudjio Ts...
Moussa BAKAYO...
Sifelani Dube
Neena Arora
Lourdes Duarte
Bertha Elizabeth ...
Crina Vicol
Yeşim Şahin
Suneel Lanka
Temitope Ogunn...
Hassan Javed N...
Carlos Albertoda...
Melissa Greta G...
Eren Esen
MOHAMED MAL...
Marco Piccini
Silvia Navarro O...
Silviu Dobrota
Micaela Denise ...
Cyprien Poucin
Siting Ni
Souha Kacem


Li-Qi Qiu
Kevin Waibel
Pamela Moyo
Jayne English
Luca Filippi
Mahlet Garedew
Olufunto Fanoro
Silvia Lucia Appl...
Kassim Badmus
Luke Woodliffe
Samar Mousa
Jennifer Hall
Farai Dziike
Laurene Petitjean
Jianfei Sun
Zhuojian Li
Naadirah Moola
Gabriela Gastelu
Jiaqi Feng
Maryna Bakume...
Denis Muvunyi
Mitra Satapathy
Fan Hsuan Liu
飞翔的大象的...
Md WasikurRahman
Raynold Techie-...
Harriet Fowler
WangZhigang
Fang Lin
José Guilherme L...
EdwardOcansey
Jerome Mwemezi
Caterina Deganutti
Mattia Annatelli
Igor Tadeu da C...
Yetar Babashova
Rémi André
Hamza Mohamed

JULY 6-10, 2020 – ONLINE

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